Lecture notes: Quantum Optics with Semiconductors and Dirac Materials

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In this series of four introductory lectures, topics at the interface of quantum optics and electronic materials will be discussed. The first lecture will introduce the concept of bandstructure and k.p theory. In the second lecture, these concepts will be applied to free optical transitions, and as an example, I will discuss optical selection rules in Dirac materials. The third lecture will introduce the concept of excitons, including Dirac excitons in relativistic materials, as well as excitons-polaritons. As a general framework for treating optical transitions in electronic materials, I will introduce the semiconductor Bloch equations in the fourth lecture.

Preamble

"One shouldnt work on semiconductors, that is a filthy mess; who knows whether any semiconductors exist."
(orig. *"Über Halbleiter soll man nicht arbeiten, das ist eine Schweinerei; wer weiss, ob es überhaupt Halbleiter gibt."*)
Wolfgang Pauli in September 1931 in a letter to Rudolf Peierls

Scope

The properties of matter can be examined through its interactions with light. A simple example is photoabsorption of an atom which reveals the energy levels of an atom. In this lecture, we are going to study the interactions between light and electrons in a solid. A class of solids which is particularly well suited for optical explorations are semiconductors, as they have a bandgap in the optical range. Typical semiconducting materials include: group IV elements of the periodic table (Si, Ge), combinations of group III and group V (such as GaAs), or combinations of group II and group VI (such as CdTe). One interesting application of semiconductors is the fabrication of microstructures which allow for confining charge carriers (electrons and/or holes) to spaces of reduced dimension: quantum wells (2D), quantum wires (1D), quantum dots (0D). In recent years, 2-dimensional confinement of electrons has also been realized in atomically thin materials: graphene (which is a semimetal, e.g. something between a metal, as it has no bandgap, and a semiconductor, as the density of states at the Fermi energy of the undopped/ungated material is zero), and transition metal dichalcogenides (TMDs), a compound of two group VI atoms ("chalcogens": S,Se,Te), and a transition metal atom (Mo,W). Bulk TMDs are well-known indirect-gap semiconductors, but only in the last ten years, it has become possible to produce isolated TMD layers. As in graphene, the low-energy behavior of electrons in the vicinity of the K-point is approximately described by the Dirac equation. In this lecture, we will study how these materials can be explored through light-matter interactions.

I. PERIODIC LATTICE

A. Definitions and basic concepts

As a starting point, we introduce a model for the solid: a perfect crystal of ions, generating a periodic electric potential for the electrons. The Hamiltonian for the electrons is given by:

$$H = \frac{1}{2m}\mathbf{p}^2 + V(\mathbf{r}) \quad \text{with} \quad V(\mathbf{r} + \mathbf{R}_n) = V(\mathbf{r}). \tag{1}$$

The vectors $\mathbf{R}_n$ are lattice vectors, i.e. $\mathbf{R}_n = \sum_i n_i \mathbf{a}_i$, with n_i being integers, and $\mathbf{a}_i$ being the vectors spanning the unit cell of the lattice (*primitive vectors*).

If the primitive vectors can be taken as the vectors connecting neighboring ions, the ions form a *Bravais lattice*. From every atomic position the lattice looks the same. We may also say that *basis* of the lattice is monoatomic. In other cases, the vectors connecting neighboring atoms are not spanning a lattice. An important example is the honeycomb lattice, which is particularly relevant for this course as it is the origin of the effective Dirac behavior in graphene and monolayer TMDs. We can still understand the structure of such an arrangement as a (Bravais) lattice, but now the basis element of the periodic structure is a two-atom basis, see Fig. 1.

The (Bravais) lattice can be characterize through its *point group symmetries* which leads to a total of 5 different lattice types in 2D, and 14 types in 3D. Point group symmetries are those coordinate transformations which leave
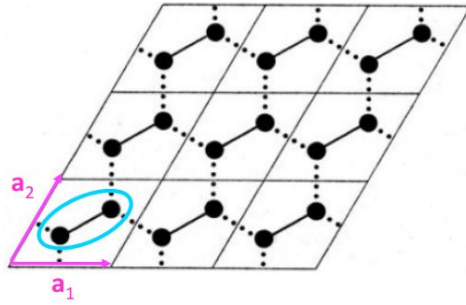
FIG. 1: Atoms forming a honeycomb structure are not the lattice points of a Bravais lattice. However, by connecting the centers of each hexagon, the structure is seen to be a Bravais lattice with a rhombic unit cell ("hexagonal lattice"). Each unit cell contains two atoms, so the basis of the lattice is biatomic.
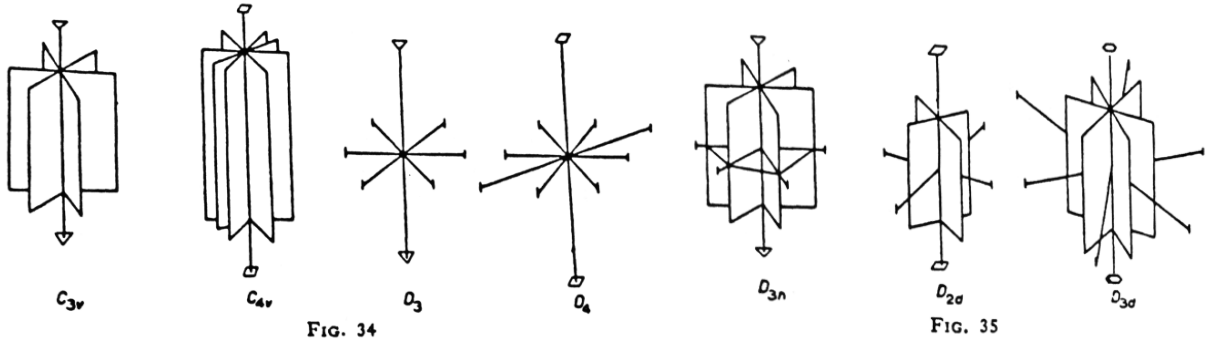

FIG. 2: Examples of some cyclic and dihedral groups. Taken from Landau/Lifshitz Vol. 3 "Quantum Mechanics", Chapter XXII.

(at least) one point unchanged. In 2D, the relevant transformations are rotations and reflections. There are different ways of denoting the different point groups. Here, we will use the *Schoenflies notation*: If there are only rotations about an axis, we have the *cyclic group* denoted by letter C_n. The index n is an integer which specifies the rotation angles $2\pi/n$ under which the system is invariant. If in addition to the n-fold rotation axis, we also have mirror planes, this is indicated through an index h or v:

C_{nh}: There is a mirror plane perpendicular to the rotation axis.

C_{nv}: There are n mirror planes which contain the rotation axis (and which are transformed into each other by the rotation).

Another important point group is the *dihedral group*, denoted by the letter D_n. As the cyclic group, it contains an n-fold rotational axis, but on top of this there are n two-fold rotational axes perpendicular to the n-fold axis. If there is a horizontal mirror symmetry, this is again expressed through an index h. Together with the two-fold rotations, this leads automatically to n vertical reflections. If there are additional vertical reflection planes which do not coincide with the two-fold rotation axis, this is denoted by an index d. Examples for cyclic and dihedral groups are illustrated in Fig. 2.

The point group symmetries of a lattice may be analyzed by looking at a unit cell, but there is not a unique choice of unit cell. Best suited for the analysis of point group symmetries is the *Wigner-Seitz cell*. It is the collection of points which are closest to a lattice point. It is obtained by connecting a lattice point with all neighboring lattice points, and drawing perpendicular intersecting lines (2D) / planes (3D) through the centers of all interconnecting lines.

B.   Bloch theorem

The Bloch theorem is the following statement: For a periodic Hamiltonian, such as Eq. (1), the eigenfunctions are of the form:

$$\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \quad \text{where} \quad u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n). \tag{2}$$
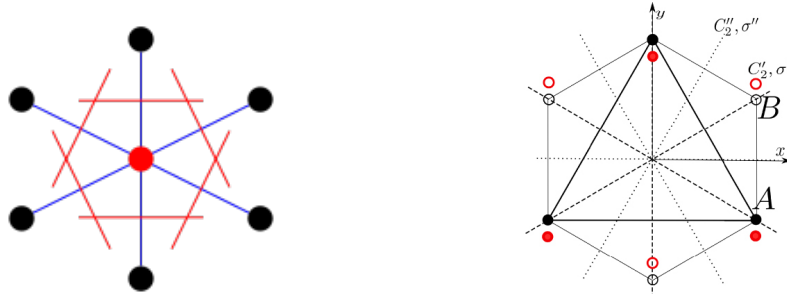
FIG. 3: The Wigner-Seitz cell of the hexagonal lattice is a hexagon. In a honeycomb arrangement of atoms (cf. Fig. 1), the Wigner-Seitz cell just goes through the 6 atoms forming a hexagon. If all atoms are the same, the point group symmetry is D_{6h} (graphene), with 6 two-fold in plane rotation axes indicated in the figure on the right. If the lattice is on top of a substrate, the two-fold rotational symmetry is lost, but the axes, together with the 6-fold axes, define mirror planes. The point group is C_{6v}. On the other hand, if the two atoms of the basis are different (as in hexagonal Boron Nitride, or as in TMDs), the symmetry is reduced D_{3h}.

The functions $u_{\mathbf{k}}(\mathbf{r})$ are called *Bloch functions*.

Proof: Consider a lattice translation T_n: $T_n \varphi_{\mathbf{k}}(\mathbf{r}) = \varphi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n)$. The Hamiltonian is invariant under this transformation: $T_n^{-1} H T_n = H$. Thus, from the Schroedinger equation we have:

$$\varphi_{\mathbf{k}}^*(\mathbf{r}) T_n^{-1} H T_n \varphi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}} |T_n \varphi_{\mathbf{k}}(\mathbf{r})|^2 = E_{\mathbf{k}} |\varphi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n)|^2, \tag{3}$$

but also

$$\varphi_{\mathbf{k}}^*(\mathbf{r}) T_n^{-1} H T_n \varphi_{\mathbf{k}}(\mathbf{r}) = \varphi_{\mathbf{k}}^*(\mathbf{r}) H \varphi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}} |\varphi_{\mathbf{k}}(\mathbf{r})|^2. \tag{4}$$

So the wave function amplitudes must be the same on lattice points:

$$|\varphi_{\mathbf{k}}(\mathbf{r})|^2 = |\varphi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n)|^2. \tag{5}$$

Thus, the functions $\varphi_{\mathbf{k}}$ must have the property:

$$\varphi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) = t_{n\mathbf{k}} \varphi_{\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad |t_{n\mathbf{k}}| = 1. \tag{6}$$

As $t_{n\mathbf{k}}$ is the eigenvalue of the lattice translation, from the property $T_{n+m} = T_n T_m$ it must also follow that

$$t_{n\mathbf{k}} t_{m\mathbf{k}} = t_{(n+m)\mathbf{k}} \tag{7}$$

The conditions for $t_{n\mathbf{k}}$ are met by the ansatz

$$t_{n\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{R}_n}. \tag{8}$$

It is then seen that a function which is periodic with the lattice [i.e. a Bloch function $u_{\mathbf{k}}(\mathbf{r})$] multiplied with $e^{i\mathbf{k}\cdot\mathbf{r}}$ provides a solution to Eqs. (6-7), which proves the Bloch theorem.

C.   Reciprocal lattice

As seen above, the wave vector $\mathbf{k}$ defines the eigenvalue t_n of $\varphi_{\mathbf{k}}$ under generic lattice translations T_n, $t_n = e^{i\mathbf{k}\cdot\mathbf{R}_n}$. But this form of the t_n immediately implies that there is a whole lattice of $\mathbf{k}$-points which are equivalent. This lattice is called the *reciprocal lattice*. It is spanned by *reciprocal lattice vectors* $\mathbf{G}$, which are defined through the condition:

$$e^{i\mathbf{k}\cdot\mathbf{R}_n} = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{R}_n}, \tag{9}$$

or simply

$$\mathbf{G}\cdot\mathbf{R}_n = 2\pi N. \tag{10}$$

Vectors $\mathbf{G}$ which fulfill this condition can be written in terms of a basis $\mathbf{b}_i$, $\mathbf{G} = \sum_i m_i \mathbf{b}_i$, for which the following relation holds:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}. \tag{11}$$

The reciprocal basis vectors can then be expressed in terms of the primitive lattice vectors as:

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)}. \tag{12}$$

The unit cell spanned by the $\mathbf{b}_j$ is called the *Brillouin zone*.

D. $\mathbf{k} \cdot \mathbf{p}$ theory

The Schroedinger equation for an electron reads

$$H\varphi_{\mathbf{k},\lambda}(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right)\varphi_{\mathbf{k},\lambda}(\mathbf{r}) = E_{\mathbf{k},\lambda}\varphi_{\mathbf{k},\lambda}(\mathbf{r}), \tag{13}$$

where λ denotes different solutions (i.e. *energy bands*). Now we apply the Bloch theorem: $\varphi_{\mathbf{k},\lambda}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k},\lambda}(\mathbf{r})$. We use the relation

$$\nabla^2\varphi_{\mathbf{k},\lambda}(\mathbf{r}) = -k^2\varphi_{\mathbf{k},\lambda}(\mathbf{r}) + 2ie^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{k}\cdot\nabla u_{\mathbf{k},\lambda}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}}\nabla^2 u_{\mathbf{k},\lambda}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}(\nabla + i\mathbf{k})^2 u_{\mathbf{k},\lambda}. \tag{14}$$

to obtain a Schroedinger equation for the Bloch functions:

$$\left(-\frac{\hbar^2}{2m}(\nabla + i\mathbf{k})^2 + V(\mathbf{r}) \right)u_{\mathbf{k},\lambda}(\mathbf{r}) = E_{\mathbf{k},\lambda}u_{\mathbf{k},\lambda}, \tag{15}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \frac{\hbar}{m}\mathbf{k}\cdot\mathbf{p} + V(\mathbf{r}) \right)u_{\mathbf{k},\lambda}(\mathbf{r}) = \left(E_{\mathbf{k},\lambda} - \frac{\hbar^2 k^2}{2m} \right)u_{\mathbf{k},\lambda}. \tag{16}$$

This expression is useful if we know the solutions to the Schroedinger equation in one special point $\mathbf{k}_0$:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \frac{\hbar}{m}\mathbf{k}_0\cdot\mathbf{p} + V(\mathbf{r}) \right)u_{\mathbf{k}_0,\lambda}(\mathbf{r}) = H_0 u_{\mathbf{k}_0,\lambda} = \epsilon_{\mathbf{k}_0,\lambda}u_{\mathbf{k}_0,\lambda}. \tag{17}$$

We define $H_1 = \frac{\hbar}{m}(\mathbf{k} - \mathbf{k}_0)\cdot\mathbf{p}$, which can be taken as a small perturbation in the vicinity of $\mathbf{k}_0$, and $\epsilon_{\mathbf{k},\lambda} = E_{\mathbf{k},\lambda} - \frac{\hbar^2 k^2}{2m}$. In lowest order, the energy is given by

$$\epsilon_{\mathbf{k},\lambda} = \epsilon_{\mathbf{k}_0,\lambda} + \sum_{\eta\neq\lambda} \frac{\langle\lambda|H_1|\eta\rangle\langle\eta|H_1|\lambda\rangle}{\epsilon_{\mathbf{k}_0,\lambda} - \epsilon_{\mathbf{k}_0,\eta}}. \tag{18}$$

Here $|\eta\rangle$ denotes the state corresponding to $\varphi_{\mathbf{k}_0,\eta}$. The matrix element $\langle\lambda|H_1|\eta\rangle = \frac{\hbar}{m}\mathbf{k}\cdot\mathbf{p}_{\lambda\eta}$, where $\mathbf{p}_{\lambda\eta} = \langle\lambda|\mathbf{p}|\eta\rangle$. Since $\mathbf{p}_{\lambda\lambda} = 0$, the lowest energy correction is second order. To first order, the energy band λ in the vicinity of $\mathbf{k}_0$ is given by

$$|\mathbf{k},\lambda\rangle = |\lambda\rangle + \frac{\hbar}{m}\sum_{\eta\neq\lambda} \frac{\mathbf{p}_{\lambda,\eta}}{\epsilon_{\mathbf{k}_0,\lambda} - \epsilon_{\mathbf{k}_0,\eta}}|\eta\rangle. \tag{19}$$

Let's assume that only two bands, $\lambda = \pm$, are relevant at the Fermi surface. We write $\langle+|\mathbf{p}|-\rangle = \sum_i p_i\mathbf{e}_i$. From Eq. (18), we find the energies of the two bands to be given by:

$$E_{\mathbf{k},\pm} = E_{\mathbf{k}_0,\pm} + \frac{\hbar^2}{2m}k^2 \pm \frac{\hbar^2}{2m}\sum_{i,j}\frac{2k_i k_j p_i^* p_j}{m\Delta} = E_{\mathbf{k}_0,\pm} + \frac{\hbar^2}{2}\left[\frac{1}{m}\sum_{i,j}\left(\delta_{ij} \pm \frac{2p_i^* p_j}{m\Delta} \right) \right]k_i k_j, \tag{20}$$

where $\Delta = \epsilon_{\mathbf{k}_0,+} - \epsilon_{\mathbf{k}_0,-}$ denotes the energy gap at $\mathbf{k}_0$. The term in the square bracket can be viewed as an *effective mass tensor*:

$$\left(\frac{1}{m_{\text{eff}}} \right)_{ij} = \frac{1}{m}\left(\delta_{ij} \pm \frac{2p_i^* p_j}{m\Delta} \right) \tag{21}$$

In isotropic cases (e.g. cubic symmetries), the effective mass becomes a scalar quantity. For the lower band (*valence band*) the effective mass can become negative (holes). For the higher band (*conduction band*), the effective mass of the electrons is often significantly lower than the free electron mass.

a.   Kane model and beyond   For group IV semiconductors, as well as III-V or II-VI compounds, the outer shell is populated by sp^3 orbitals. The conduction band at $k = 0$ (Γ-point) consists of an s-electron, while three p-electrons form a degenerate valence band. In terms of angular momentum quantum numbers:

$$|s\rangle = |l = 0, m = 0\rangle, \tag{22}$$
$$|p_{x,y,z}\rangle = |l = 1, m = \pm 1, 0\rangle. \tag{23}$$

The selection rule $\langle l, m|\mathbf{p}|l', m'\rangle \propto \delta_{l,l'\pm 1}\delta_{m,m'}$ dictates the form of the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian:

$$H_{\mathbf{k}\cdot\mathbf{p}} = H_0 + H_1 = \begin{pmatrix} E_0 & 0 & 0 & Ak \\ 0 & E_1 & 0 & 0 \\ 0 & 0 & E_1 & 0 \\ Ak & 0 & 0 & E_1 \end{pmatrix} \tag{24}$$

So in this model (*Kane model*), two bands at E_1 are not modified, e.g. their effective mass will be positive, while (for these bands to be valence bands), they should be negative. To cure this failure, one has to take into account (i) spin-orbit coupling which splits off one valence band, (ii) the effect of other than the sp^3 bands. An effective model, which takes into account the effect of other bands through three phenomenological parameters, is the *Luttinger model*. This model takes into account 4 valence bands at $j = \pm 3/2$ (eigenvalue to the operator $\mathbf{L} + \mathbf{S}$): $|3/2, \pm 3/2\rangle$, $|3/2, \pm 1/2\rangle$. The spin-orbit coupling splits the bands at $j = 1/2$ to lower energies. The four valence bands are degenerate at the Γ-point, but split into two degenerate pairs away from $k = 0$, the heavy holes ($m_j = \pm 3/2$) and the light holes ($m_j = \pm 1/2$).

b.   TMDs   Let us next apply the $\mathbf{k.p}$ method to TMD monolayers [see also Kormanyos et al., Phys. Rev. B 88, 0454416 (2013)]. From first-principle calculations (DFT), it is known that the VB is dominated at the $\pm K$ points by orbitals $d_{x^2-y^2}$ and d_{xy} of the transition metal atom. In the CB, the band edge is dominated by d_{z^2}. To improve the model, let us look for other orbitals which may be important. To this aim, the analysis of symmetries and group theory are important tools.

*S*ymmmetry: The group of the wave vector (i.e. the group of symmetry operations which leaves the wave vector unchanged) is C_{3h} for K, and D_{3h} for Γ. In the following, we will restrict ourselves to the K-point. C_{3h} is an Abelian group containing the idenity, threefold rotations, a horizontal mirror plane, and the corresponding rotation-reflections. It has 6 (one-dimensional) irreducible representations (IRs): $A', A'', E_1', E_2', E_1'', E_2''$. As a reminder: a representation of the group is a set of functions which is mapped onto itself under the group transformations. If this set can be divided into smaller sets with this property, the representation is "reducible". In contrast, irreducible representations cannot be divided into smaller representations. The transformation behavior of an irreducible representation (described by the character table) is characteristic of the representation, and representations with identical characters are equivalent.

The VB is found to transform as A', whereas the CB transforms as E_1'. Thus, just as the in-plane momentum, both CB and VB are even under σ_h. States which are odd under σ_h do not couple to them on the $\mathbf{k.p}$ level. The next bands with the even horizontal mirror plane symmetry are CB+2 and VB-3 (both transforming as E_2'). The corresponding four-band model is given by, with real-valued parameters γ:

$$H_{\mathbf{k.p}} = \begin{pmatrix} \epsilon_{\mathrm{v},K} & \gamma_3 q_- & \gamma_2 q_+ & \gamma_4 q_+ \\ \gamma_3 q_+ & \epsilon_{\mathrm{c},K} & \gamma_5 q_- & \gamma_6 q_- \\ \gamma_2 q_- & \gamma_5 q_+ & \epsilon_{\mathrm{v}-3,K} & 0 \\ \gamma_4 q_- & \gamma_6 q_+ & 0 & \epsilon_{\mathrm{c}+2,K} \end{pmatrix} \tag{25}$$

Here, we have defined $q_\pm = k_x \pm i k_y$ and $p_\pm = p_x \pm i p_y$. The form of the k.p Hamiltonian is dictated by the symmetries. For instance, under C_3, we have the transformation of $p_\pm$ given by:

$$C_3^\dagger p_\pm C_3 = e^{\mp i 2\pi/3} p_\pm, \tag{26}$$

whereas states from the IRs transform as

$$C_3|\Psi_{A'}\rangle = |\Psi_{A'}\rangle, \tag{27}$$
$$C_3|\Psi_{E_1'}\rangle = e^{+i2\pi/3}|\Psi_{E_1'}\rangle, \tag{28}$$
$$C_3|\Psi_{E_2'}\rangle = e^{-i2\pi/3}|\Psi_{E_2'}\rangle. \tag{29}$$
$$\tag{30}$$

From this, we get, for instance, $\langle c|p_+|v\rangle = \langle c|C_3 C_3^\dagger p_+ C_3 C_3^\dagger|v\rangle = e^{-i4\pi/3}\langle c|p_+|v\rangle$, and thus $\langle c|p_+|v\rangle = 0$.

Let us only mention that the same Hamiltonian, with q_+ and q_- exchanged, is found at the $-K$ point. So, one may also define $q_\pm = k_x \pm i\tau k_y$, with $\tau = \pm 1$ being a valley index.

Finally, as we are interested in the physics of the VB and CB, we may reduce this 4-band Hamiltonian to a 2-band model via the *Loewdin partitioning technique*. This technique takes into account the effect of the other levels in a perturbative way. The lowest order simply neglects the other bands, and we get the massive Dirac equation:

$$H_{\mathbf{k.p}}^{(1)} = \begin{pmatrix} \epsilon_{v,K} & \gamma_3 q_- \\ \gamma_3 q^+ & \epsilon_{c,K} \end{pmatrix} \tag{31}$$

The second-order contribution, with $m, m' \in \{1, 2\}$, is written as

$$H_{m,m'}^{(2)} = \frac{1}{2} \sum_{l \in \{3,4\}} H_{m,l} H_{l,m'} \left[\frac{1}{E_m - E_l} + \frac{1}{E_{m'} - E_l} \right]. \tag{32}$$

This leads to the following qualitatively distinct terms:

$$H_{\mathbf{k.p}}^{(2)} = \begin{pmatrix} \alpha q^2 & 0 \\ 0 & \beta q^2 \end{pmatrix} + \kappa \begin{pmatrix} 0 & q_+^2 \\ q_-^2 & 0 \end{pmatrix}. \tag{33}$$

The first term takes into account the fact that electrons and holes have different effective masses. The second term destroys the isotropy of the Dirac model, and accounts for the trigonal warping (= trigonal shape of isoenergy contours) which is due to the C_3 crystal structure. The parameters $\gamma_3, \alpha, \beta, \kappa$ and the band-edge energies can be evaluated using Kohn-Sham orbitals (not so good results), or fitted to the DFT band (good results - even better when also one cubic term in k is taken into account, e.g. third-order Loewdin).

So far, *spin-orbit coupling* has been neglected. The simplest way to take it into account is within the *atomic approximation*, by adding a term:

$$H_{\text{SOC}} = \lambda \mathbf{L} \cdot \mathbf{S}. \tag{34}$$

Here, we only mention the following observations related to spin-orbit coupling:

- Strong spin-orbit coupling of the $d_{x^2-y^2}$ and d_{xy} orbitals in the transition metal leads to strong spin-orbit coupling effects at the band edge of the valence band (in contrast to the VB band edge, and in contrast to graphene which is lacking strong spin-orbit coupling).

- Since the operator $L\pm = L_x \pm iL_y$ is odd under σ_h, it is not enough to take into account only the four bands used above, but also the other bands in between with odd σ_h symmetry should be taken into account.

- After Loewdin partitioning, to lowest order the Hamiltonian has the form:

$$H = \gamma_3(\tau k_x \sigma_x + k_y \sigma_y) + \frac{\epsilon_{c,K} - \epsilon_{v,K}}{2}\sigma_z - \lambda\tau\frac{\sigma_z - 1}{2}s_z, \tag{35}$$

where the σ-matrices take into account the band degree of freedom, whereas s_z represents the spin degree of freedom.

E.   Tight-binding approximation

The validity of the **k.p** method tends to be limited to a restricted region of k-space. We finalize this section by briefly discussing an alternative approach, the *tight-binding approximation*. The idea behind this method is that the electrons remain close to the atomic sites. Therefore, let $\Phi_\lambda(\mathbf{r} - \mathbf{R}_l)$ be a solution to the atomic Schroedinger equation (i.e. with $V(\mathbf{r} - \mathbf{R}_l)$ being the potential of a single atom at point $\mathbf{R}_l$):

$$\left(\frac{-\nabla^2}{2m} + V(\mathbf{r} - \mathbf{R}_l) \right) \Phi_\lambda(\mathbf{r} - \mathbf{R}_l) \equiv H_l \Phi_\lambda(\mathbf{r} - \mathbf{R}_l) = \epsilon_\lambda \Phi_\lambda(\mathbf{r} - \mathbf{R}_l). \tag{36}$$

The tight-binding ansatz (which also fulfills the Bloch theorem!) is given by:

$$\Psi_{\mathbf{k},\lambda}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n} \Phi_\lambda(\mathbf{r} - \mathbf{R}_n). \tag{37}$$

Let us now approximately evaluate the band energies $E_{\mathbf{k},\lambda}$ from this ansatz:

$$E_{\mathbf{k},\lambda} = \frac{\int d^D r \Psi^*_{\mathbf{k},\lambda}(\mathbf{r}) H \Psi_{\mathbf{k},\lambda}(\mathbf{r})}{\int d^D r \Psi^*_{\mathbf{k},\lambda}(\mathbf{r}) \Psi_{\mathbf{k},\lambda}(\mathbf{r})}. \tag{38}$$

We approximately have $\int d^D r \Phi^*_\lambda(\mathbf{r}+\mathbf{R}_m)\Phi_\lambda(\mathbf{r}+\mathbf{R}_n) = \delta_{m,n}$, so the denominator is evaluated as N/V, i.e. the inverse of the size of a unit cell. The numerator we write in the following way:

$$\mathcal{N} = \frac{1}{V}\sum_{n,m} e^{i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_m)}\mathcal{I}_{n,m}, \quad \text{where}$$

$$\mathcal{I}_{n,m} = \int d^D r \, \Phi^*_\lambda(\mathbf{r}-\mathbf{R}_m)\left[H_n + \sum_{l\neq n} V(\mathbf{r}-\mathbf{R}_l)\right]\Phi_\lambda(\mathbf{r}-\mathbf{R}_n) =$$

$$= \epsilon_\lambda \delta_{n,m} + \sum_{l\neq n} \int d^D r \, \Phi^*_\lambda(\mathbf{r}-\mathbf{R}_m)V(\mathbf{r}-\mathbf{R}_l)\Phi_\lambda(\mathbf{r}-\mathbf{R}_n). \tag{39}$$

And we write:

$$E_{\mathbf{k},\lambda} = \frac{1}{N}\sum_{n,m}\left(\mathcal{I}_{n,n}\delta_{n,m} + \mathcal{I}_{n,n\pm 1}\delta_{n\pm 1,m} + \dots\right) \tag{40}$$

The different integrals $\mathcal{I}_{n,m}$, i.e. on-site shift, nearest-neighbor overlaps, next-nearest neighbor overlaps, etc. have to be computed numerically.

   a. Example: We conclude with an example for a TMD (MoS$_2$), as taken from G. Liu et al., Phys. Rev. B 88, 085433 (2013). In this paper a three-band model for TMDs is derived using the tight-binding method. By taking into account terms up to 3NN-hopping, the model appears to be quantitatively satisfactory within the full Brillouin zone.

   As in the section before, symmetry analysis comes into play when setting up the model. The three atomic states to build the tight-biding wave function are d_{z^2}, $d_{x^2-y^2}$, and d_{xy}. The point group of the system is D_{3h}, and d_{z^2} belong to the 1D IR A'_1, whereas $d_{x^2-y^2}$, and d_{xy} to the 2D IR E'. In the following, these two IRs are denoted by the indext $j = 1, 2$. A second index $\mu = 1$ (for $j = 1$) or $\mu = 1, 2$ (for $j = 2$) denotes the states $|\Phi^j_\mu(\mathbf{r})\rangle$.

   The overlap integrals for a given vector $\mathbf{R}$ of the molybdenum lattice are:

$$E^{j,j'}_{\mu\mu'}(\mathbf{R}) = \langle \Phi^j_\mu(\mathbf{r})|H|\Phi^{j'}_{\mu'}(\mathbf{r}-\mathbf{R})\rangle. \tag{41}$$

Although there are six different lattice vectors connecting nearest neighbors, we need to evaluate this expression only for one of them. The other overlap integrals are obtained from symmetry properties:

$$\text{Let} \quad \mathbf{R}' = \hat{g}_n \mathbf{R} \quad \text{with} \quad \hat{g}_n \in D_{3h} \quad \Rightarrow \quad E^{j,j'}(\mathbf{R}') = D^j(\hat{g}_n)E^{j,j'}(\mathbf{R})[D^{j'}(\hat{g}_n)]^\dagger, \tag{42}$$

where $D^j(\hat{g}_n)$ is the matrix for the transformation $\hat{g}_n$ acting on the jth IR of the group D_{3h}.

   In fact, instead of trying to evaluate the integrals $E^{j,j'}_{\mu\mu'}(\mathbf{R})$, one may take their value as a fitting parameter. In this way, symmetry helps to keep the number of fitting parameters as low as possible (6 instead of 36 for every hopping order + 2 for the on-site energies).

   By expanding the three-band tight-binding model at the K-point and applying Loewdin partitioning to reduce it to a two-band model, one obtains in lowest order the massive Dirac equation.

II. BAND-TO-BAND TRANSITIONS OF FREE ELECTRONS

A. Minimal coupling

Classical light-matter interactions are described by the Lorentz force

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v}\times\mathbf{B}), \tag{43}$$

with $\mathbf{E}, \mathbf{B}$ being the electric and magnetic field, and $\mathbf{v}$ the velocity of a particle with charge q. Invoking scalar and vector potentials Φ and $\mathbf{A}$, the Lorentz force is obtained from an Euler-Lagrange equation, $\mathbf{F} = (-\nabla + \frac{d}{dt}\nabla_{\mathbf{v}})U$ with a potential:

$$U = q(\Phi - \mathbf{v}\cdot\mathbf{A}). \tag{44}$$

To check this explicitly, we may choose to work in the Coulomb gauge:

$$\nabla \cdot \mathbf{A} = 0 \;\Rightarrow\; \Phi = 0 \;\text{ (in absence of charges) }\; \Rightarrow\; \mathbf{E} = -\frac{\partial}{\partial t}\mathbf{A}, \;\; \mathbf{B} = \nabla \times \mathbf{A}. \tag{45}$$

Also note that $\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{A} = \frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla)\mathbf{A}$, and $\nabla(\mathbf{v} \cdot \mathbf{A}) = \mathbf{v} \times (\nabla \times \mathbf{A}) + (\mathbf{v} \cdot \nabla)\mathbf{A}$.

The corresponding Lagrangian $L = m\mathbf{v}^2/2 - U$ yields a Hamiltonian $H = \mathbf{p} \cdot \mathbf{v} - L$, with

$$\mathbf{p} = \frac{\mathrm{d}L}{\mathrm{d}\mathbf{v}} = m\mathbf{v} + q\mathbf{A}, \tag{46}$$

so we explicitly have:

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\Phi. \tag{47}$$

In the Coulomb gauge, $\Phi = 0$ and we have the "minimal coupling" obtained by replacing $\mathbf{p} \to \mathbf{p} - q\mathbf{A}$ which can be done within both classical and quantum theories.

B. Electric dipole approximation

The form of light-matter interaction from the minimal coupling description is:

$$H_{\mathrm{LM}} = -\frac{q}{2m}(\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) + \frac{q^2}{2m}\mathbf{A}^2. \tag{48}$$

For a plane-wave, we have

$$\mathbf{A}(\mathbf{r}, t) = A_0\hat{\epsilon} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{c.c.}, \tag{49}$$

where $\hat{\epsilon}$ is the polarization, ω the frequency, and $\mathbf{k}$ the wave vector of the light field. We may expand this in $\mathbf{k}$:

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k} \cdot \mathbf{r} + \dots, \tag{50}$$

and by dropping all but the first term, we obtain what is known as the *dipole approximation*. Essentially, this approximation is justified by the fact that (typically) the light field varies on scales λ much larger than the length scale relevant for the electron dynamics (e.g. lattice constants in a crystal).

Under this approximation, the $\mathbf{A}^2$ term in Eq. (48) becomes a constant and can be dropped. In the Coulomb gauge, we also have $\mathbf{p} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{p}$. With this, we have:

$$H_{\mathrm{LM}} = -\frac{2qA_0}{m}\hat{\epsilon} \cdot \mathbf{p} \cos(\omega t). \tag{51}$$

Now we use the following which is valid for a general single-particle Hamiltonian $\mathcal{H}_0$:

$$\mathbf{p} = -\frac{im}{\hbar}[\mathbf{r}, \mathcal{H}_0]. \tag{52}$$

We get:

$$H_{\mathrm{LM}} = \frac{2iqA_0}{\hbar}\hat{\epsilon} \cdot [\mathbf{r}, \mathcal{H}_0] \cos(\omega t). \tag{53}$$

Having in mind electrons in a crystal, eigenstates of $\mathcal{H}_0$ are denoted $|\lambda, \mathbf{k}\rangle$ at energies $E_{\lambda,\mathbf{k}}$. Thus we find

$$\langle\lambda, \mathbf{k}|H_{\mathrm{LM}}|\lambda', \mathbf{k}'\rangle = \frac{2iqA_0}{\hbar}(E_{\lambda',\mathbf{k}'} - E_{\lambda,\mathbf{k}})\langle\lambda, \mathbf{k}|\mathbf{r}|\lambda', \mathbf{k}'\rangle \cos(\omega t) \tag{54}$$

Since $\mathbf{E}(t) = -\partial_t\mathbf{A}(t)$, we have $A_0 = i/(2\omega)E_0$, so we can also write

$$\langle\lambda, \mathbf{k}|H_{\mathrm{LM}}|\lambda', \mathbf{k}'\rangle = E_0\hat{\epsilon}\cos(\omega t) \cdot q\langle\lambda, \mathbf{k}|\mathbf{r}|\lambda', \mathbf{k}'\rangle\frac{E_{\lambda',\mathbf{k}'} - E_{\lambda,\mathbf{k}}}{\hbar\omega} = \mathbf{E}(t) \cdot \mathbf{d}_{\lambda\mathbf{k},\lambda'\mathbf{k}'}\frac{E_{\lambda',\mathbf{k}'} - E_{\lambda,\mathbf{k}}}{\hbar\omega}. \tag{55}$$

Here, $\mathbf{d}_{\lambda\mathbf{k},\lambda'\mathbf{k}'} = q\langle\lambda, \mathbf{k}|\mathbf{r}|\lambda', \mathbf{k}'\rangle$ is the electric dipole moment between the states $|\lambda', \mathbf{k}'\rangle$ and $|\lambda, \mathbf{k}\rangle$. For a resonant absorption process, we have $E_{\lambda',\mathbf{k}'} - E_{\lambda,\mathbf{k}} = -\omega$, and the light-matter Hamiltonian takes the familiar form:

$$H_{\mathrm{LM}} = -\mathbf{d} \cdot \mathbf{E}(t), \tag{56}$$

where $\mathbf{d} = q\mathbf{r}$.

C. Linear response, susceptibility, oscillator strength, f-sum rule

To determine the behavior of an electron in an optical field, we need to solve the time-dependent Schrödinger equation:

$$i\hbar\partial_t\Psi(\mathbf{r},t) = (H + H_{\text{LM}})\Psi(\mathbf{r},t), \tag{57}$$

with H being the crystal Hamiltonian from Eq. (1), and H_{LM} being the light-matter interaction, for which, for simplicity reasons, we assume the dipole approximation, $H_{\text{LM}} = -\mathbf{d}\cdot\mathbf{E}(t)$.

The crystal eigenfunctions $\varphi_{\lambda,\mathbf{k}}(\mathbf{r})$ at energies $E_{\lambda,\mathbf{k}}$ provide an orthonormal basis to expand the function $\Psi(\mathbf{r},t)$:

$$\Psi(\mathbf{r},t) = \sum_{\lambda,\mathbf{k}} a_{\lambda,\mathbf{k}}(t)e^{-iE_{\lambda,\mathbf{k}}t}\varphi_{\lambda,\mathbf{k}}(\mathbf{r}). \tag{58}$$

The coefficients $a_{\lambda,\mathbf{k}}(t)$ are defined through a set of coupled first-order differential equations:

$$i\hbar\dot{a}_{\lambda,\mathbf{k}}(t) = -\mathbf{E}(t)\cdot\sum_{\lambda',\mathbf{k}'}\mathbf{d}_{\lambda\mathbf{k},\lambda'\mathbf{k}'}e^{-i(E_{\lambda',\mathbf{k}'}-E_{\lambda,\mathbf{k}})t}a_{\lambda',\mathbf{k}'}(t). \tag{59}$$

One can solve this set of equation iteratively in different orders of $\mathbf{E}$. The zero-order "solution" $a_{\lambda,\mathbf{k}}^{(0)}$ is given by the initial conditions, which are then plugged into the r.h.s. of Eq. 59:

$$i\hbar\dot{a}_{\lambda,\mathbf{k}}^{(1)}(t) = -\mathbf{E}(t)\cdot\sum_{\lambda',\mathbf{k}'}\mathbf{d}_{\lambda\mathbf{k},\lambda'\mathbf{k}'}e^{i(E_{\lambda',\mathbf{k}'}-E_{\lambda,\mathbf{k}})t}a_{\lambda',\mathbf{k}'}^{(0)}(t). \tag{60}$$

Integrating these equations yields the *linear response* of the crystal electron to the optical field.

Let us assume that the system is initialized (in the infinite past $t\to-\infty$) in an eigenstate at $\mathbf{k}=\mathbf{k}_0$ and $\lambda=\lambda_0$. Within linear response approximation, the amplitude to be in another level $|\lambda,\mathbf{k}\rangle$ at a later time t is given by:

$$a_{\lambda,\mathbf{k}}(t) = -\frac{1}{i\hbar}\int_{-\infty}^t \mathrm{d}t'\,\mathbf{E}(t')\cdot\mathbf{d}_{\lambda\mathbf{k},\lambda_0\mathbf{k}_0}e^{-i(E_{\lambda_0,\mathbf{k}_0}-E_{\lambda,\mathbf{k}})t'}. \tag{61}$$

To evaluate this integral, we write

$$\mathbf{E}(t) = \lim_{\gamma\to 0}\int\frac{\mathrm{d}\omega}{2\pi}\,\mathbf{E}(\omega)e^{-i\omega t}e^{\gamma t}, \tag{62}$$

where the infinitesimal γ insures convergence. We obtain:

$$a_{\lambda,\mathbf{k}}(t) = -\frac{\mathbf{d}_{\lambda\mathbf{k},\lambda'\mathbf{k}'}}{\hbar}\int\frac{\mathrm{d}\omega}{2\pi}\,\mathbf{E}(\omega)\frac{e^{-i(\omega+\Delta_{\lambda'\mathbf{k}',\lambda\mathbf{k}})t}}{\omega+\Delta_{\lambda'\mathbf{k}',\lambda\mathbf{k}}+i\gamma}. \tag{63}$$

The wave function reads

$$\Psi(\mathbf{r},t) = e^{-iE_{\lambda_0,\mathbf{k}_0}t}\left[\varphi_{\lambda_0,\mathbf{k}_0}(\mathbf{r}) - \sum_{\lambda,\mathbf{k}}\frac{\mathbf{d}_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}}}{\hbar}\varphi_{\lambda,\mathbf{k}}(\mathbf{r})\int\frac{\mathrm{d}\omega}{2\pi}\mathbf{E}(\omega)\frac{e^{-i\omega t}}{\omega+\Delta_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}}+i\gamma}\right] + \mathcal{O}(\mathbf{E}^2). \tag{64}$$

With this, let us evaluate the electronic polarization along the polarization vector of the field $\hat{\epsilon}$, and the corresponding susceptibility. For the moment, we take these quantities to be microscopic, i.e. derived for a single electron. The macroscopic version of these quantities can simply be obtained by summing over all the microscopic polarizations or microscopic susceptibilities. We will explicitly carry out this sum a little later, after we have convinced ourselves that the dipole matrix element is diagonal in $\mathbf{k}$. The microscopic polarization is defined as

$$\mathcal{P}(t) = \int \mathrm{d}\mathbf{r}\,\Psi^*(\mathbf{r},t)(\mathbf{d}\cdot\hat{\epsilon})\Psi(\mathbf{r},t), \tag{65}$$

which to linear order in $\mathbf{E}$ reads:

$$\mathcal{P}(t) = -\sum_{\lambda,\mathbf{k}}\frac{|\hat{\epsilon}\cdot\mathbf{d}_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}}|^2}{\hbar}\int\frac{\mathrm{d}\omega}{2\pi}\left[E_0(\omega)\frac{e^{-i\omega t}}{\omega+\Delta_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}}+i\gamma}+\text{c.c.}\right] \overset{!}{=} \int\frac{\mathrm{d}\omega}{2\pi}\mathcal{P}(\omega)e^{-i\omega t}. \tag{66}$$

Using the fact that $E_0^*(\omega) = E_0(-\omega)$, we can use the above equation to determine the linear susceptibility $\chi(\omega)$:

$$\mathcal{P}(\omega) = \chi(\omega)E_0(\omega) \Rightarrow \chi(\omega) = -\frac{1}{\hbar}\sum_{\lambda,\mathbf{k}}|\hat{\epsilon}\cdot\mathbf{d}_{\lambda_0\mathbf{k}_0,\lambda,\mathbf{k}}|^2\left(\frac{1}{\omega + \Delta_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}} + i\gamma} - \frac{1}{\omega - \Delta_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}} + i\gamma}\right). \tag{67}$$

We can interpret this expression as a sum over various susceptibilities from various harmonic oscillators at resonance frequency $\omega_0 \equiv \Delta_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}}/\hbar$, i.e. between level $|\lambda_0\mathbf{k}_0\rangle$ and any other level. The susceptibility of a harmonic oscillator with mass m_0 and resonance frequency ω_0 reads:

$$\chi_{\text{H.O.}}(\omega) = -\frac{e^2}{2m_0\omega_0}\left(\frac{1}{\omega - \omega_0 + i\gamma} - \frac{1}{\omega + \omega_0 + i\gamma}\right). \tag{68}$$

So by interpreting each electronic transition as an oscillator, each transition contributes to the total susceptibility with a corresponding *oscillator strength* $f_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}}$ such that $\chi(\omega) = \sum_{\mathbf{k},\lambda} f_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}} \chi_{\text{H.O.}}$. So the oscillator strength is given by:

$$f_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}} = \frac{2m_0}{e^2\hbar}|\hat{\epsilon}\cdot\mathbf{d}_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}}|^2\Delta_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}}. \tag{69}$$

To simplify the notation, let us in the following drop the index $\mathbf{k}$, and choose coordinates such that $\hat{\epsilon} = \hat{x}$. From Eq. (69), we have

$$\sum_\lambda f_{\lambda_0,\lambda} = \frac{2m_0}{\hbar}\langle\lambda|x|\lambda_0\rangle\langle\lambda_0|x|\lambda\rangle(E_\lambda - E_{\lambda_0}). \tag{70}$$

With $|\lambda\rangle$ being eigenfunctions of H, we have:

$$\langle\lambda_0|x|\lambda\rangle(E_\lambda - E_{\lambda_0}) = -\frac{1}{\hbar}\langle\lambda_0|[H,x]|\lambda\rangle, \tag{71}$$

and

$$\langle\lambda|x|\lambda_0\rangle(E_\lambda - E_{\lambda_0}) = \frac{1}{\hbar}\langle\lambda|[H,x]|\lambda_0\rangle, \tag{72}$$

so we have

$$\sum_\lambda f_{\lambda_0,\lambda} = -\frac{2m_0}{\hbar^2}\langle\lambda_0|[H,x]x|\lambda_0\rangle = \frac{2m_0}{\hbar^2}\langle\lambda_0|x[H,x]|\lambda_0\rangle. \tag{73}$$

It must follow that

$$\sum_\lambda f_{\lambda_0,\lambda} = \frac{m_0}{\hbar^2}\langle\lambda_0|[x,[H,x]]|\lambda_0\rangle. \tag{74}$$

Since $[x,[x,H]] = [x,\frac{i\hbar}{m_0}p_x] = \frac{\hbar^2}{m_0}$, we obtain the f-sum rule:

$$\sum_\lambda f_{\lambda_0,\lambda} = 1. \tag{75}$$

In words: The strength of all dipole transitions of a free carrier is a constant.

D. Dipole selection rules

We have seen that, within the dipole approximation, the light-matter Hamiltonian is given by $H_{\text{LM}}(t) = -\mathbf{d}\cdot\mathbf{E}(t)$, where the dipole moment $\mathbf{d}$ for a transition from $\lambda'\mathbf{k}'$ to $\lambda\mathbf{k}$ is given by

$$\mathbf{d}_{\lambda'\mathbf{k}',\lambda\mathbf{k}} = e\langle\lambda'\mathbf{k}'|\mathbf{r}|\lambda\mathbf{k}\rangle = \frac{1}{E_{\lambda\mathbf{k}} - E_{\lambda'\mathbf{k}'}}\langle\lambda'\mathbf{k}'|[\mathbf{r},H]|\lambda\mathbf{k}\rangle = \frac{i}{m(E_{\lambda\mathbf{k}} - E_{\lambda'\mathbf{k}'})}\langle\lambda'\mathbf{k}'|\mathbf{p}|\lambda\mathbf{k}\rangle. \tag{76}$$

So the same matrix element and the same selection rules which are relevant for the **k.p** theory also determine the optical dipole transitions.

Making the Bloch ansatz

$$\varphi_{\lambda\mathbf{k}}(\mathbf{r}) = \langle\mathbf{r}|\lambda\mathbf{k}\rangle = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{\lambda\mathbf{k}}(\mathbf{r}), \tag{77}$$

we obtain

$$\langle\lambda'\mathbf{k}'|\mathbf{p}|\lambda\mathbf{k}\rangle = \frac{1}{V}\int \mathrm{d}^D r \; e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}u_{\lambda'\mathbf{k}'}^*(\mathbf{r})(\hbar\mathbf{k}+\mathbf{p})u_{\lambda\mathbf{k}}(\mathbf{r}). \tag{78}$$

Now we split the integral over the full space into an integral over a unit cell and a sum over lattice sites, and use the periodicity of the Bloch functions:

$$\langle\lambda'\mathbf{k}'|\mathbf{p}|\lambda\mathbf{k}\rangle = \sum_{n=1}^{N}\frac{e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_n}}{N}\int_{\text{cell}} \mathrm{d}^D r\frac{e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}}{v_{\text{cell}}}u_{\lambda'\mathbf{k}'}^*(\mathbf{r})(\hbar\mathbf{k}+\mathbf{p})u_{\lambda\mathbf{k}}(\mathbf{r}). \tag{79}$$

The sum yields $\delta_{\mathbf{k}',\mathbf{k}}$, so the electron momentum is conserved. This is a consequence of the dipole approximation which essentially sets the photon momentum to zero (in comparison to the electron momentum). The exponential term then vanishes from the unit cell integral, and due to the orthonormality of the Bloch function, the $\mathbf{k}$ disappears. We have:

$$\langle\lambda'\mathbf{k}'|\mathbf{p}|\lambda\mathbf{k}\rangle = \delta_{\mathbf{k}',\mathbf{k}}\mathbf{p}_{\lambda'\mathbf{k},\lambda\mathbf{k}} \approx \delta_{\mathbf{k}',\mathbf{k}}\mathbf{p}_{\lambda',\lambda}, \tag{80}$$

where in the last step we disregard the dependence of the momentum operator on $\mathbf{k}$, e.g. we set $\mathbf{p}_{\lambda',\lambda} = \mathbf{p}_{\lambda'\mathbf{0},\lambda\mathbf{0}}$ (i.e. lowest order **k.p** theory).

First, we use this result to evaluate the macroscopic polarization and macroscopic susceptibility. We simply take the microscopic results from the previous section, Eqs. (66) and (67), and replace $\sum_{\mathbf{k}}\mathbf{d}_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}}$ by $\mathbf{d}_{\lambda_0\mathbf{k}_0,\lambda\mathbf{k}_0} = d_{\lambda_0,\lambda}$. If we make a two-level approximation, we can also remove the sum in λ, and the transition dipole is simply $\mathbf{d}_{\text{vc}}$. If the thermal probability of a level $\mathbf{k}$ being occupied in the valence (conduction) band is $f_{\mathbf{kv}}$ ($f_{\mathbf{kc}}$), the macroscopic polarization/suscetibility is given by summing over all $\mathbf{k}$ and weighting with $(f_{\mathbf{kv}} - f_{\mathbf{kc}})$:

$$\mathcal{P}(\omega) = E_0(\omega)\frac{\hat{\epsilon}\cdot\mathbf{d}_{\text{vc}}}{\hbar}\frac{1}{\omega+\Delta_{\mathbf{k}}+i\gamma}\left(f_{\mathbf{kv}} - f_{\mathbf{kc}}\right). \tag{81}$$

Second, we derive the dipole selection rules. They are determined by the symmetries of the bands. For a light field with a fixed polarization $\hat{\epsilon}$, we need to evaluate the components $\hat{\epsilon}\cdot\mathbf{p}_{\lambda',\lambda}$ to see if, for the given polarization, the transition is dipole-allowed or not. For instance, for circularly polarized light we have $\hat{\epsilon}_\sigma = \mathbf{e}_x + i\sigma\mathbf{e}_y$, so we need to look at $p_{\lambda',\lambda}^x + \sigma i p_{\lambda',\lambda}^y = p_{\lambda',\lambda}^\sigma$.

Example: Fundamental transition in TMD monolayer (i.e. direct transitions at $\pm K$-point).

From the discussion of the **k.p** theory, we recall that at the $\pm K$-point the point group symmetry is C_{3h} with six 1D IRs. The conduction band is essential given by the $|d_{z^2}\rangle$ orbital of the transition metal atom, which transforms as E_1'. The valence bands are given by $(|d_{x^2-y^2}\rangle \pm i|d_{xy}\rangle)/\sqrt{2}$, and thus transform as A' at the K-point, and E_2' at the $-K$ point. The transformation properties of these IRs in combination with the transformation properties of $p_\pm$ have dictated the form of the **k.p** Hamiltonian in the τK-point:

$$H_{\mathbf{k.p}}^\tau = \begin{pmatrix} \Delta/2 & \gamma k_\tau \\ \gamma k_{-\tau} & -\Delta/2 \end{pmatrix} = \begin{pmatrix} \Delta/2 & \gamma k e^{i\tau\Phi_{\mathbf{k}}} \\ \gamma k e^{-i\tau\Phi_{\mathbf{k}}} & -\Delta/2 \end{pmatrix} \tag{82}$$

with $k_\tau = k_x + i\tau k_y$. Exactly the same considerations which lead to the form of $H_{\mathbf{k.p}}^\tau$ also imply

$$\langle c,\tau|p_+(\mathbf{e}_x + i\mathbf{e}_y) + p_-(\mathbf{e}_x - i\mathbf{e}_y)|v,\tau\rangle \sim \langle c,\tau|p_\tau(\mathbf{e}_x + i\sigma\mathbf{e}_y)|v,\tau\rangle. \tag{83}$$

So for the dipole matrix element corresponding to p_σ to be non-zero, σ has to match with the valley index τ. Or, in other words, a transition due to a circular polarization σ can only occur in valley $\tau = \sigma$. That means that the circular polarization of the light can be used to address one of the two valleys. For this reason, TMDs are interesting materials in the context of "valleytronics".

It is interesting and easy to go beyond this lowest level description which is strictly valid only at the $\pm K$ points. The winding of the Bloch function around the $\pm K$ points is then seen to have an impact onto the selection rules

which is relevant for excitonic transitions (to be discussed in the next lecture). The solutions of the Dirac equation $H^\tau \phi_{\pm,\mathbf{k}} = \pm E_{\mathbf{k}} \phi_{\pm,\mathbf{k}}$ are of the form:

$$\phi_{+,\mathbf{k}} = \begin{pmatrix} \cos(\theta_k/2) \\ e^{i\Phi_\mathbf{k}} \sin(\theta_k/2) \end{pmatrix}, \qquad \phi_{-,\mathbf{k}} = \begin{pmatrix} e^{-i\Phi_\mathbf{k}} \sin(\theta_k/2) \\ -\cos(\theta_k/2) \end{pmatrix}, \tag{84}$$

So $\langle \phi_{+,\mathbf{k}} | p_+ | \phi_{-,\mathbf{k}} \rangle \sim -\cos^2(\theta_k/2)$, whereas $\langle \phi_{+,\mathbf{k}} | p_- | \phi_{-,\mathbf{k}} \rangle \sim e^{-2i\Phi_\mathbf{k}} \sin^2(\theta_k/2)$. While the p_+ transition is much stronger (k is small!), it has no dependence on the angular part of $\mathbf{k}$. It therefore leads to transitions which conserve angular momentum. Contrarily, the weak p_- obtain an angular momentum dependence due to the winding of the Bloch functions. References: Pu Gong et al. PRB 95, 125420 (2017). Ting Cao et al. PRL 120, 087402 (2018). Xiaoou Zhang et al., PRL 120, 0777401 (2018).

E. Fermi's golden rule

Fermi's golden rule provides a measure for the transition probability between eigenstates of an unperturbed Hamiltonian H_0 due to a (potentially time-dependent) perturbation $H_1(t)$. The transition rate $\Gamma_{i \to f}$ is given by:

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} |\langle f | H_1(t) | i \rangle|^2 \delta(E_f - E_i - \omega), \tag{85}$$

assuming that there is a single state at E_i and a final states at E_f, and ω being the frequency of the sinusoidal perturbation. It is straightforward to dervie this rule from time-dependent Schroedinger equation.

$$H|\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle. \tag{86}$$

We assume that $H = H_0 + H_1 \exp(i\omega t)$, and expand $\Psi(t)$ in the eigenbasis of H_0. The dynamics of the coefficients $a_k(t)$ is governed by

$$i\hbar \frac{da_k(t)}{dt} = \sum_n \langle k | H_1 | n \rangle a_n(t) \exp[i(E_k - E_n - \hbar\omega)/\hbar], \tag{87}$$

We linearize (with respect to the (weak!) perturbation) this set of equation by replacing $a_n(t)$ (which at $t > 0$ depends on H_1) by $a_n(0)$ (which does not depend on H_1). Since we are interested in transitions from level i, we have $a_n(0) = \delta_{n,i}$. We can then immediately integrate the differential equation:

$$i\hbar a_k(t) = 2\langle k | H_1 | i \rangle e^{i\omega' t/2} \frac{\sin \omega' t/2}{\omega'}, \tag{88}$$

where $\omega' = E_k/\hbar - E_i/\hbar - \omega$. From this, we get

$$\Gamma_{i \to k} = \frac{d}{dt} |a_k(t)|^2 = \frac{2|\langle k | H_1 | i \rangle|^2}{\hbar^2} \frac{\sin \omega' t}{\omega'}. \tag{89}$$

For small enough $\omega' t$, one can replace $\sin(\omega' t)/\omega'$ by t, so the transition amplitude is linear in time.

If an isolated initial state is coupled to a continuum, we may ask for the transition probability as a function of the driving frequency ω. In the above expression, we replace $\langle k|$ by $\langle E|\rho(E)$, with $\rho(E)$ being the density of states, and integrate in E (or in $\omega' = E/\hbar - E_i/\hbar - \omega$). For the δ-function, there is the following identity:

$$\delta(x) = \lim_{\epsilon \to 0} \frac{\sin(x/\epsilon)}{\pi x}, \tag{90}$$

so at large t we get a $\pi\delta(\omega')$. We end up with

$$\Gamma(\omega) = \frac{2\pi |\langle E_i + \hbar\omega | H_1 | i \rangle|^2}{\hbar} \rho(E_i + \hbar\omega). \tag{91}$$

III. EXCITONS

In the previous lectures, we considered only non-interacting electrons. This has led to the notion of bandstructure in the crystal. By coupling to light, we can excite band-to-band transition. They leave an empty state in the valence band, i.e. a hole, and a filled state in the conduction band, i.e. a particle. Attractive Coulomb interactions between particle and hole can lead to bound states (excitons) which are the subject of this lecture.

A. Coulomb interactions and second quantized Hamiltonian

For the Coulomb Hamiltonian in a crystal, we write down a density-density type of interactions in Fourier space. It consists of three terms: interactions between the electrons, interactions between the nuclei, interactions between electrons and nuclei.

$$H_C = \frac{1}{2} \sum_{\mathbf{q}} W_{\mathbf{q}} \left(\rho_{-\mathbf{q},\text{el}} \rho_{\mathbf{q},\text{el}} + \rho_{-\mathbf{q},\text{ion}} \rho_{\mathbf{q},\text{ion}} + 2\rho_{-\mathbf{q},\text{el}} \rho_{\mathbf{q},\text{ion}} \right). \tag{92}$$

We note that this expression includes a self-interactions which we may exclude at a later point.

Let us first discuss the Fourier coefficients of the Coulomb potential, $W_{\mathbf{q}}$. They depend on the dimension of the system. The simplest case is for 2D, as we can do the Fourier transformation straightforwardly:

$$W_{\mathbf{q}} = \frac{1}{\epsilon} \int d\mathbf{r} \; e^{i\mathbf{q}\cdot\mathbf{r}}/r = \frac{1}{\epsilon} \int dr \int d\phi e^{iqr\cos\phi} = \frac{2\pi}{\epsilon} \int dr J_0(qr) = \frac{2\pi}{\epsilon q}. \tag{93}$$

In 3D, the Fourier integral $\int d\mathbf{r} \; e^{i\mathbf{q}\cdot\mathbf{r}} \frac{1}{r}$ does not converge, but we may apply a little trick. We look at a Yukawa-type of potential, $\frac{1}{r}e^{-\gamma r}$, which vanishes faster than $1/r$, and thus converges. Physically, this is a screened Coulomb potential, and we can (after Fourier transforming) take the limit of zero screening, $\gamma \to 0$. We get $W_{\mathbf{q}} \sim q^{-2}$.

In 1D, the Coulomb potential is pathological, as it has a short-range divergence. It can be remedied if we think of a 1D system as a 3D system which has been frozen along two directions (e.g. the wave functions have no dynamics in these coordinates, but are just some envelope functions). We integrate the potential with the envelope functions over these frozen directions to obtain an effective 1D potential. This quasi-1D potential is free from the divergence which a true 1D Coulomb potential would have. In real space, such quasi-1D potential has the form $1/(r + \gamma R)$.

The charge densities of electrons and nuclei are expressed in the following way

$$\rho_{\mathbf{q},\text{el}} = -\frac{|e|}{V} \sum_{i=1}^{N} e^{-i\mathbf{q}\cdot\mathbf{r}_i} \qquad \text{and} \qquad \rho_{\mathbf{q},\text{ion}} = \frac{|e|N}{V} \delta_{\mathbf{q},0}. \tag{94}$$

The expression for the electrons charge density follows from a distribution of N discrete charges at positions $\mathbf{r}_i$. Since we don't want to consider the nuclei positions as degrees of freedom, we take their charge density as a homogeneous background. It is made of N positive charges (equal to the number of electrons), so in total there is charge neutrality. With this, the ion-electron and ion-ion interactions contribute only at $\mathbf{q} = 0$, but exactly in such a way that together with the electron-electron interactions at $\mathbf{q} = 0$ all terms at $\mathbf{q} = 0$ cancel. That's very lucky, because the divergence of $W_{\mathbf{q}}$ at $\mathbf{q} = 0$ is removed from the Hamiltonian:

$$H_C = \frac{e^2}{2} \sum_{i,j,\mathbf{q}\neq 0} W_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)}. \tag{95}$$

This expression also makes it evident where the self-energy comes in: it corresponds to terms with $i = j$. If we exclude the self-energy (by excluding the terms with $i = j$), we arrive at the *jellium model*:

$$H_C = \frac{1}{2} \sum_{\mathbf{q}\neq 0} W_{\mathbf{q}} (L^6 \rho_{-\mathbf{q},\text{e}} \rho_{\mathbf{q},\text{e}} - e^2 N). \tag{96}$$

Here we have re-expressed everything in terms of densities, and the second term comes from the exclusion of terms with $j = i$.

As we now go from single-particle to few- or even many-particle physics, it is convenient to introduce second quantized expressions. In second quantization, particles are described by fields. The field operator $\hat{\Psi}_s^\dagger(\mathbf{r})$ creates an electron in spin state s at position $\mathbf{r}$. We can expand the field operator in any single-particle basis, e.g. a basis given by the bands in the crystal:

$$\hat{\Psi}_s(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\lambda,\mathbf{k}} \hat{a}_{\lambda,\mathbf{k},s} e^{i\mathbf{k}\cdot\mathbf{r}} u_{\lambda,\mathbf{k},s}(\mathbf{r}), \tag{97}$$

where $a_{\lambda,\mathbf{k},s}$ annihilates an electron of spin s in band λ at wave vector $\mathbf{k}$. Obviously, this is a well-suited expansion, when we deal with crystal electrons. It also contains, as a special case, the electron gas: Just demand there is only one band, with Bloch functions $u_{\lambda,\mathbf{k}} = 1$.

The one-particle density operator is given by:

$$\hat{\rho}(\mathbf{r}) = -|e| \sum_s \hat{\Psi}_s^\dagger(\mathbf{r})\hat{\Psi}_s(\mathbf{r}) = -\frac{|e|}{V} \sum_s \sum_{\lambda,\lambda'} \sum_{\mathbf{k},\mathbf{k}'} u_{\lambda,\mathbf{k}}^*(\mathbf{r}) u_{\lambda',\mathbf{k}'}(\mathbf{r}) e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \hat{a}_{\lambda\mathbf{k}s}^\dagger \hat{a}_{\lambda'\mathbf{k}'s}, \tag{98}$$

which Fourier transforms into

$$\hat{\rho}_\mathbf{q} = -\frac{|e|}{V} \sum_s \sum_{\lambda,\lambda'} \sum_\mathbf{k} \hat{a}_{\lambda\mathbf{k}s}^\dagger \hat{a}_{\lambda'(\mathbf{k}+\mathbf{q})s} \mathcal{F}_{\lambda\lambda'}(\mathbf{k},\mathbf{k}+\mathbf{q}). \tag{99}$$

Here, we have introduced the form factor $\mathcal{F}$ defined as

$$\mathcal{F}_{\lambda\lambda'}(\mathbf{k},\mathbf{k}') = \int_{\text{cell}} \mathrm{d}\mathbf{r}\, u_{\lambda\mathbf{k}}^*(\mathbf{r}) u_{\lambda'\mathbf{k}'}(\mathbf{r}). \tag{100}$$

In general, evaluation of the form factors is a difficult task. However, to lowest order in $\mathbf{k}.\mathbf{p}$ theory, we replace the Bloch functions $u_{\lambda\mathbf{k}}(\mathbf{r})$ by the function at the band edge $u_{\lambda\mathbf{k}_0}(\mathbf{r})$. Then, we obtain $\mathcal{F}_{\lambda\lambda'}(\mathbf{k},\mathbf{k}') = \delta_{\lambda,\lambda'}$.

Let us finally by write all Hamiltonian parts in terms of annihilation/creation operators (suppressing spin for brevity). Plugging Eq. (97) into Eq. (96), we obtain for the Coulomb interactions:

$$H_C = \frac{e^2}{2} \sum_{\mathbf{q}\neq 0} W_\mathbf{q} \left(\sum_{\{\lambda_i\}} \sum_{\mathbf{k},\mathbf{k}'} \hat{a}_{\lambda_1\mathbf{k}}^\dagger \hat{a}_{\lambda_4,\mathbf{k}+\mathbf{q}} \hat{a}_{\lambda_2,\mathbf{k}'}^\dagger \hat{a}_{\lambda_3,\mathbf{k}'-\mathbf{q}} \mathcal{F}_{\lambda_1\lambda_4} \mathcal{F}_{\lambda_2\lambda_3} - N \right). \tag{101}$$

By normal-ordering the first term, and replacing the form factors by Kronecker-δs, the second term is cancelled:

$$H_C = \frac{e^2}{2} \sum_{\mathbf{q}\neq 0} W_\mathbf{q} \sum_{\lambda,\lambda'} \sum_{\mathbf{k},\mathbf{k}'} \hat{a}_{\lambda\mathbf{k}}^\dagger \hat{a}_{\lambda',\mathbf{k}'}^\dagger \hat{a}_{\lambda',\mathbf{k}'-\mathbf{q}} \hat{a}_{\lambda,\mathbf{k}+\mathbf{q}}. \tag{102}$$

With our choice of basis, the single-electron Hamiltonian reads

$$H_0 = \sum_{\mathbf{k},\lambda} E_{\lambda,\mathbf{k}} \hat{n}_{\lambda,\mathbf{k}} = \sum_{\mathbf{k},\lambda} E_{\lambda,\mathbf{k}} \hat{a}_{\lambda,\mathbf{k}}^\dagger \hat{a}_{\lambda,\mathbf{k}}. \tag{103}$$

The light-matter Hamiltonian in dipole approximation is given by

$$H_{\text{LM}} = -E_0(t) \sum_{\lambda,\lambda'} \sum_\mathbf{k} \left(\hat{\epsilon} \cdot \mathbf{d}_{\lambda,\lambda'} \hat{a}_{\lambda,\mathbf{k}}^\dagger \hat{a}_{\lambda'\mathbf{k}} + \text{h.c.} \right), \tag{104}$$

where the $\mathbf{k}$-dependence of the interband dipole element $\mathbf{d}_{\lambda,\lambda'}$ has been suppressed.

B. Wannier equation

Let us now consider a two-band system (conduction band c, valence band v), and study the dynamics of the interband polarization:

$$\mathbf{P}(t) \equiv \int \mathrm{d}\mathbf{r}\, \langle \hat{\Psi}(\mathbf{r})^\dagger e\mathbf{r}\Psi(\mathbf{r}) \rangle = \sum_{\mathbf{k},\mathbf{k}'} \langle \hat{a}_{c,\mathbf{k}}^\dagger \hat{a}_{v,\mathbf{k}'} \rangle \times e \int \mathrm{d}\mathbf{r}\, \mathbf{r}\, u_{c\mathbf{k}}^*(\mathbf{r}) u_{v\mathbf{k}'}(\mathbf{r}) e^{i\mathbf{r}\cdot(\mathbf{k}-\mathbf{k}')} \approx \sum_\mathbf{k} \langle \hat{a}_{c,\mathbf{k}}^\dagger \hat{a}_{v,\mathbf{k}} \rangle \mathbf{d}_{cv}. \tag{105}$$

In the second step, we have introduced the interband dipole moment $\mathbf{d}_{cv}$, which may be approximated by a constant (i.e. no $\mathbf{k}$-dependence). Moreover, the second step takes into account that the integration over space yields a Kronecker-delta in $\mathbf{k}$.

We see that the polarization is determined by the pair function $P_{vc,\mathbf{k}}(t) = \langle a_{v,\mathbf{k}}^\dagger a_{c,\mathbf{k}} \rangle$. Its dynamics is governed by the following Heisenberg equation of motion (lengthy calculation):

$$\hbar \left[i\frac{d}{dt} - (E_{c,k} - E_{v,k}) \right] P_{vc,\mathbf{k}}(t) = [n_{c,\mathbf{k}}(t) - n_{v,\mathbf{k}}(t)] \mathbf{d}_{cv} \cdot \hat{\epsilon} E_0(t) + \sum_{\mathbf{k}',\mathbf{q}} V_q \Big(\langle \hat{a}_{c,\mathbf{k}'+\mathbf{q}}^\dagger \hat{a}_{v,\mathbf{k}-\mathbf{q}}^\dagger \hat{a}_{c,\mathbf{k}'} \hat{a}_{c,\mathbf{k}} \rangle$$

$$+ \langle a_{v,\mathbf{k}'+\mathbf{q}}^\dagger a_{v,\mathbf{k}-\mathbf{q}}^\dagger \hat{a}_{v,\mathbf{k}'} \hat{a}_{c,\mathbf{k}} \rangle + \langle a_{v,\mathbf{k}}^\dagger a_{c,\mathbf{k}'-\mathbf{q}}^\dagger \hat{a}_{c,\mathbf{k}'} \hat{a}_{c,\mathbf{k}-\mathbf{q}} \rangle + \langle a_{v,\mathbf{k}}^\dagger a_{v,\mathbf{k}'-\mathbf{q}}^\dagger \hat{a}_{v,\mathbf{k}'} \hat{a}_{c,\mathbf{k}-\mathbf{q}} \rangle \Big) \tag{106}$$

For the interactions terms, we do a random phase approximation (RPA), i.e. we decompose the 4-operator product into 2-operator products, but disregard those decompositions which do not yield a term which is proportional to $n_{v,\mathbf{k}} = a_{v,\mathbf{k}}^\dagger a_{v,\mathbf{k}}$ or $n_{c,\mathbf{k}} = a_{c,\mathbf{k}}^\dagger a_{c,\mathbf{k}}$. This means that we get terms of the form

$$\langle a_{v,\mathbf{k}}^\dagger a_{v,\mathbf{k}'-\mathbf{q}}^\dagger \hat{a}_{v,\mathbf{k}'} \hat{a}_{c,\mathbf{k}-\mathbf{q}} \rangle \approx P_{vc,\mathbf{k}-\mathbf{q}} n_{v,\mathbf{k}} \delta_{\mathbf{k},\mathbf{k}'}, \tag{107}$$

i.e. terms which are diagonal in $\mathbf{k}$. If we consider $n_v = 1$, such terms can be included in the energy of the band as self-energies.

There are also non-diagonal terms of the form:

$$\langle a_{v,\mathbf{k}'+\mathbf{q}}^\dagger a_{v,\mathbf{k}-\mathbf{q}}^\dagger \hat{a}_{v,\mathbf{k}'} \hat{a}_{c,\mathbf{k}} \rangle \approx P_{vc,\mathbf{k}} n_{v,\mathbf{k}-\mathbf{q}} \delta_{\mathbf{k}'+\mathbf{q},\mathbf{k}}. \tag{108}$$

These terms will explicitly remain in the equation of motion, which after RPA reads:

$$\hbar \left[i\frac{d}{dt} - (\epsilon_{c,k} - \epsilon_{v,k}) \right] P_{vc,\mathbf{k}}(t) = [n_{c,\mathbf{k}}(t) - n_{v,\mathbf{k}}(t)] \left[\mathbf{d}_{cv} \cdot \hat{\epsilon} E_0(t) + \sum_{\mathbf{q} \neq \mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} P_{vc,\mathbf{q}} \right].$$

So the equation of motion for the pair function depends on the dynamics of the populations $n_{\lambda,\mathbf{k}}(t)$. We will study this set of equations of motion later, in the lecture about Semiconductor Bloch Equations. For now, let us assume that the populations are in thermal equilibrium. Then we write:

$$n_{\lambda\mathbf{k}} = f_{\lambda,\mathbf{k}} = \frac{1}{1 + e^{\beta(\epsilon_{\lambda\mathbf{k}} - E_{\mathrm{F}})}} \tag{109}$$

This approximation leads to a linear resposne theory. With Eq. (109), we then have a single, first-order differential equation for $P_{cv}(t)$, which can straightforwardly integrated for free electrons ($V_\mathbf{k} = 0$) via a Fourier transform to frequency space. We get:

$$P_{vc}^{\mathrm{free}}(\omega) = (f_{v,\mathbf{k}} - f_{c,\mathbf{k}}) \, \mathbf{d}_{cv} \cdot \hat{\epsilon} E_0(\omega) \frac{1}{\hbar[\omega + i\delta - (\epsilon_{c,k} - \epsilon_{v,k})]}. \tag{110}$$

In the presence of interactions, the equation reads:

$$[\hbar(\omega + i\delta) - (\epsilon_{c,k} - \epsilon_{v,k})] P_{cv,\mathbf{k}}(\omega) + \delta f_{cv,\mathbf{k}} \sum_{\mathbf{q} \neq \mathbf{k}} V_{|\mathbf{q}-\mathbf{k}|} P_{vc,\mathbf{k}}(\omega) = -\delta f_{cv,\mathbf{k}} \mathbf{d}_{cv} \cdot \hat{\epsilon} E_0(\omega). \tag{111}$$

In the following, we set the population difference $\delta f_{cv,\mathbf{k}} = f_{v,\mathbf{k}} - f_{c,\mathbf{k}}$ to 1, i.e. we consider an unexcited semiconductor. Within the effective mass approximation, we may write

$$\epsilon_{c,k} - \epsilon_{v,k} = E_{\mathrm{gap}} + \frac{\hbar^2 k^2}{2\mu}, \tag{112}$$

where μ is the reduced mass, $\mu^{-1} = m_c^{-1} - m_v^{-1}$, and E_{gap} denotes the bandgap energy. Remind that the positive effective mass of the holes is $-m_v$.

Now it is convenient to transform into real space. Replace $f_\mathbf{k} = (1/L)^D \int d\mathbf{r} f(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$, and integrate/sum in $\mathbf{k}$. Note that

$$\int d\mathbf{k} \, k^2 P_{vc,\mathbf{k}} = (1/L)^D \int d\mathbf{k} \int d\mathbf{r} \, k^2 P_{vc}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} = (1/L)^D \int d\mathbf{k} \int d\mathbf{r} \, P_{vc}(\mathbf{r})(-\nabla_\mathbf{r}^2) e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$= (1/L)^D \int d\mathbf{k} \int d\mathbf{r} \, e^{i\mathbf{k}\cdot\mathbf{r}}(-\nabla_\mathbf{r}^2) P_{vc}(\mathbf{r}). \tag{113}$$

The last step is obtained by partial integration. The terms which appear as a constant in the $\mathbf{k}$-space equation, $\mathbf{d}_{cv} \cdot \hat{\epsilon} E_0(\omega)$, acquire a Dirac-$\delta$, $\delta(\mathbf{r})$, when transformed in real space. Note that this comes from neglecting the structure of the Bloch functions. For the interaction term, we get:

$$\sum_\mathbf{k} \sum_{\mathbf{q} \neq \mathbf{k}} \int d\mathbf{r} \int d\mathbf{r}' \, V(r) e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}} P_{vc,\mathbf{k}} e^{i\mathbf{q}\cdot\mathbf{r}'} \sim \sum_\mathbf{k} \int d\mathbf{r} \, e^{i\mathbf{k}\cdot\mathbf{r}} V(r) P_{vc}(\mathbf{r}). \tag{114}$$

So the equation we get in real space reads:

$$\left[\hbar(\omega + i\delta) - E_{\text{gap}} + \frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2\mu} + V(r) \right] P_{vc}(\mathbf{r}) = -\mathbf{d}_{vc} \cdot \hat{\epsilon} E_0(\omega) \delta(\mathbf{r}) L^3. \tag{115}$$

For $E_0 = 0$, this equation is homogeneous, but in the presence of an electric field it is an inhomogeneous differential equation. In such case, it is common to first solve the homogeneous equation, and expand the solution of the inhomogeneous equation in the homogeneous solutions. The homogeneous part is the *Wannier equation*. Let's write $\omega = E_{\text{gap}} + E_\nu$, and replace $P_{vc}(\mathbf{r})$ by $\Psi_\nu(\mathbf{r})$, an electron-hole wave function. We get:

$$-\left(\frac{\hbar^2 \nabla^2}{2\mu} + V(r) \right) \Psi_\nu(\mathbf{r}) = E_\nu \Psi_\nu(\mathbf{r}). \tag{116}$$

That is essentially the equation for hydrogen atom, so the relevant units for length and energy are the Bohr radius a_0 and the Rydberg Ry. They are given by:

$$Ry = \frac{\hbar^2}{2\mu a_0^2}, \quad a_0 = \frac{\hbar^2 \epsilon}{e^2 \mu}. \tag{117}$$

As compared to the Rydberg energy and the Bohr radius in the context of the hydrogen atom (free electron in vacuum), here we have to consider the reduced mass given by the effective band masses (for instance in GaAs about an order of magnitude smaller than the electron rest mass), and a modified electric constant due to a dielectric ($\epsilon_d = 12.8$ in GaAs). So the smaller mass and the larger dielectric constant lead to an increase of the Bohr radius, roughly two orders of magnitude, and a decrease of the Rydberg roughly three orders of magnitude. Instead of $Ry = 13.6 eV$, we have $Ry = 4 meV$ in GaAs.

The solution of the Wannier equation is obtained by diving $\nabla_{\mathbf{r}}^2$ in a radial and an angular part. The angular part is solved immediately by spherical harmonic $Y_{l,m}(\phi, \theta)$ in 3D, or simply an exponential $e^{im\phi}$ in 2D. The energies E_ν are fully determined by the radial part of the wave function (i.e. on this level we have no fine structure). As we also know from the hydrogen problem, there are two types of solution: The better known solutions are the ones at negative energy, which are discrete bound states (i.e. the different orbitals 1s, 2s, 2p, 3s, 3p, 3d,...). But there are also solutions at positive energy, i.e. the ionization continuumn.

The bound states provide a possibility to resonantly excite the system at an energy below the bandgap. These resonances are given by a Rydberg series, as it is known from atomic physics:

$$E_n = -Ry \frac{1}{n^2} \qquad \text{in 3D}, \tag{118}$$

$$E_n = -Ry \frac{1}{(n + 1/2)^2} \qquad \text{in 2D}. \tag{119}$$

C. Optical properties

Explicit expression for optical properties of the material are obtained by solving the inhomogeneous equation of motion, i.e. Eq. (115).

After obtaining the homogeneous solutions $\Psi_\nu(\mathbf{r})$ of the Wannier equation, we write

$$P_{vc}(\mathbf{r}) = \sum_\nu b_\nu \Psi_\nu(\mathbf{r}), \tag{120}$$

which we insert into the inhomogeneous Eq. (115). We multiply by $\Psi_\mu^*(\mathbf{r})$ and integrate over $\mathbf{r}$, in order to obtain an equation for the coefficients b_μ:

$$b_\mu = -\frac{\mathbf{d} \cdot \hat{\epsilon} E_0(\omega) L^D \Psi_\mu^*(\mathbf{0})}{\hbar(\omega + i\delta) - E_{\text{gap}} - E_\mu}. \tag{121}$$

So from this expression we immediately see that the pair function is only determined by exciton solutions which vanish at $\mathbf{r} = \mathbf{0}$, due to the dipole approximation and neglection of band structure. It is easy to relate the pair function to the optical polarization and the optical susceptibility, $\mathbf{P}(\omega) = \sum_{\mathbf{k}}(P_{cv,\mathbf{k}}\mathbf{d}_{cv} + \text{c.c.}) = \chi(\omega)\hat{\epsilon} E(\omega)$. Explicitly, we obtain:

$$\chi(\omega) = -2|\mathbf{d}_{cv}|^2 \sum_\mu |\Psi_\mu(\mathbf{0})|^2 \left[\frac{1}{\hbar(\omega + i\delta) - E_{\text{gap}} - E_\nu} - \frac{1}{\hbar(\omega + i\delta) + E_{\text{gap}} + E_\nu} \right]. \tag{122}$$
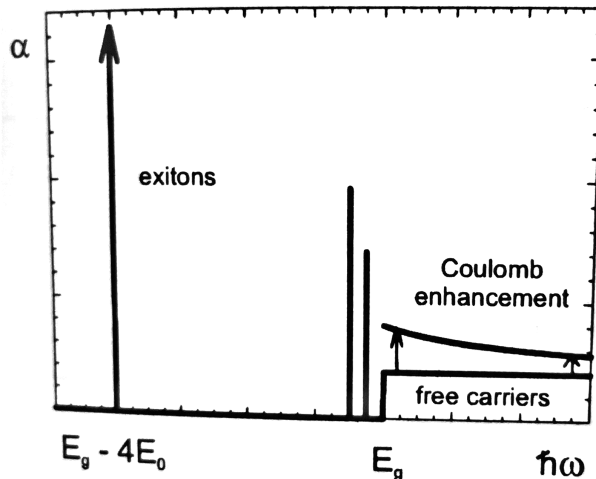
FIG. 4: Sketch of absorption vs. frequency for 2d semiconductor: Discrete absorption lines in the band gap due to exciton bound states (1s, 2s, 3s, with spacing given by Rydberg series, and quickly decaying height (Elliott formula). Sommerfeld enhancement of the absorption continuum. Taken from: Haug and Koch, "Quantum Theory of the Optical and Electronic Properties of Semiconductors", 2nd ed. (2004).

The second term is non-resonant, so it is often neglected. From this expression, one can also derive an expression for the absorption coefficient. By plugging in the wave functions, one obtains the so-called *Elliott formula*. Without writing it down, let us just mention that Elliot formula tells us that absorption consists of a series of sharp lines $\sim \delta(\omega - (E_{\text{gap}} - E_n))$, which rapidly decrease in height ($\sim n^{-2}$ in 3D, $(n+1/2)^{-3}$ in 2D), followed by the continuum part above the bandgap energy. This continuum part can be compared to the absorption coefficient which one would obtain for free electrons, and the so-called Coulomb enhancement (or Sommerfeld enhancement) is found.

D. Excitons in TMDs

Although the framework discussed above is very general, at certain points approximations/assumptions were made, which actually depend on the concrete material. The discussion so far is valid for "conventional" semiconductor systems.

The main things which need to be reconsidered in the context of Dirac materials are the following:

- The term proportional to ∇^2 in the Wannier equations stems from band energies assumed to have a quadratic dispersion. For gapped Dirac material, this assumption is still correct, but one needs to change in the context of graphene.

- The interaction potential has been taken as a bare Coulomb potential. However, in a 2D system one should take into account that electromagnetic fields are not confined to the planar system, but also go through a dielectric medium surrounding the electronic system. The Keldysh potential is suited to take into account the effect of dielectric environment:

$$V(r) = \frac{\pi e^2}{2\epsilon r_0} \left[H_0(r/r_0) \right] - Y_0(r/r_0) \right] \quad \text{or} \quad V_{\mathbf{q}} = \frac{2\pi e^2}{\epsilon q} \frac{1}{1 + r_0 q}. \tag{123}$$

Here, H_0 and Y_0 are Struve and Bessel functions of the second kind, and r_0 is material-specific screening parameter, and the dielectric constant $\epsilon = 4\pi\epsilon_0\epsilon_d$ also depends on the 2D material and its environment. A reference on this choice of potential is: Cudazzo, Tokatly, and Rubio. PRB 84 0855406 (2011). Asymptotically, the Keldysh potential goes like $1/r$ for $r \to \infty$, but as $\log(r)$ for $r \to 0$.

One effect which is due to this potential is the splitting of 2s and 2p states, with 2p being at lower energy (i.e. stronger bound excitons).

- No matter whether the Coulomb or the Keldysh potential is used to describe interactions, the band structure of the crystals generally leads to further modifications of the effective interactions. They are taken into account by the form factors $\mathcal{F}_{\lambda,\lambda'}$, see Eq. (100). We have set these form factors to one (i.e. effective mass approximation assuming that electrons are like free particles), but in a Dirac material the electrons are described by Dirac spinors, so the form factors actually play a role. Therefore, in Eqs. (109) and (111), we have to replace $V_{|\mathbf{k}-\mathbf{q}|}$ by $V_{|\mathbf{k}-\mathbf{q}|}\mathcal{F}_{cc}(\mathbf{k},\mathbf{k}-\mathbf{q})\mathcal{F}_{vv}(\mathbf{k}-\mathbf{1},\mathbf{k})$.

  With these form factors, the winding of the Bloch spinor around $\pm K$ are taken into account, and reflect in a splitting of the otherwise degenerate $2p^+$ and $2p-$ levels.

- For the inhomogeneous part in Eqs. (109) or (111), proportional to the dipole moment between the two bands, we have neglected any $\mathbf{k}$-dependence. This leads to a $\delta(\mathbf{r})$ in real space, restricts the excitonic states which are optically bright to the s-orbitals. However, we have seen that the dipole matrix in a Dirac material has two contributions: one which depends only on k, and a second (weaker) one which also has angular dependence on $\mathbf{k}$ (again, due to the winding of the Bloch spinors!). Within a single valley, these two contributions correspond to opposite circular polarization of the light. But also in the case of fixed circular polarization, both contributions coexist, but stem from opposite valleys (spin-orbit coupling which lifts the degeneracies between valleys may allow for individually suppressing one or the other contribution!)

IV. SEMICONDUCTOR BLOCH EQUATIONS

In this lecture, we will reconsider the equation of motion for the band polarization, which we already studied in the context of free electron transitions as well as excitons (i.e. electron transitions in the presence of Coulomb interactions). But in contrast to our earlier approaches, now we will avoid the approximations which restrict the dynamics to linear response. This will lead to a set of coupled equations, known as the semiconductor Bloch equations.

A. Electron-hole system

We start with introducing the concept of hole. In many circumstances, it is convenient to map the electronic annihilation and creation operators in the valence band onto holes:

$$h_{\mathbf{k},s}^\dagger \equiv a_{v,-\mathbf{k},-s}, \quad e_{\mathbf{k},s}^\dagger \equiv a_{c,\mathbf{k},s}^\dagger \tag{124}$$

i.e. the annihilation of a VB electron with momentum $-\mathbf{k}$ and spin $-s$ is equivalent to the creation of a hole at momentum $\mathbf{k}$ and spin s.

Let us consider a few Hamiltonian terms under this electron-hole transformation:

$$\sum_{\mathbf{k}} E_{v,\mathbf{k}} a_{v,\mathbf{k}}^\dagger a_{v,\mathbf{k}} = \sum_{\mathbf{k}} E_{v,\mathbf{k}} h_{-\mathbf{k}} h_{-\mathbf{k}}^\dagger = \sum_{\mathbf{k}} E_{v,\mathbf{k}} (1 - h_{-\mathbf{k}}^\dagger h_{-\mathbf{k}}) = E_0 + \sum_{\mathbf{k}} \tilde{E}_{h,\mathbf{k}} h_{\mathbf{k}}^\dagger h_{\mathbf{k}}, \tag{125}$$

$$\sum_{\mathbf{k},\mathbf{k}'} \sum_{\mathbf{q}\neq\mathbf{0}} V_q a_{v,\mathbf{k}+\mathbf{q}}^\dagger a_{v,\mathbf{k}'-\mathbf{q}}^\dagger a_{v,\mathbf{k}'} a_{v,\mathbf{k}} = \sum_{\mathbf{k},\mathbf{k}'} \sum_{\mathbf{q}\neq\mathbf{0}} V_q h_{-\mathbf{k}-\mathbf{q}} h_{-\mathbf{k}'+\mathbf{q}} h_{-\mathbf{k}'}^\dagger h_{-\mathbf{k}}^\dagger = \sum_{\mathbf{k},\mathbf{k}'} \sum_{\mathbf{q}\neq\mathbf{0}} V_q \left(h_{\mathbf{k}'}^\dagger h_{\mathbf{k}}^\dagger h_{\mathbf{k}+\mathbf{q}} h_{\mathbf{k}'-\mathbf{q}} - 2h_{\mathbf{k}}^\dagger h_{\mathbf{k}} \right), \tag{126}$$

$$\sum_{\mathbf{k},\mathbf{k}'} \sum_{\mathbf{q}\neq\mathbf{0}} V_q a_{c,\mathbf{k}+\mathbf{q}}^\dagger a_{v,\mathbf{k}'-\mathbf{q}}^\dagger a_{v,\mathbf{k}'} a_{c,\mathbf{k}} = \sum_{\mathbf{k},\mathbf{k}'} \sum_{\mathbf{q}\neq\mathbf{0}} V_q e_{\mathbf{k}+\mathbf{q}}^\dagger h_{-\mathbf{k}'+\mathbf{q}} h_{-\mathbf{k}'}^\dagger e_{\mathbf{k}} = -\sum_{\mathbf{k},\mathbf{k}'} \sum_{\mathbf{q}\neq\mathbf{0}} V_q e_{\mathbf{k}+\mathbf{q}}^\dagger h_{\mathbf{k}'-\mathbf{q}}^\dagger h_{\mathbf{k}'} e_{\mathbf{k}} \tag{127}$$

So in the single-particle energy, the transformation just leads to an additional constant term E_0 which we may neglect. The interactions in the valence band give rise to an exchange interaction $-\sum_{\mathbf{q},\mathbf{k}} V_q n_{h,\mathbf{k}}$, which we may take into account in the band energy of the holes:

$$\tilde{E}_{h,\mathbf{k}} \to E_{h,\mathbf{k}} = \tilde{E}_{h,\mathbf{k}} - \sum_{\mathbf{q}} V_q. \tag{128}$$

Importantly, the interactions between bands appear with the opposite sign, because they now reflect attraction between the negative charges in the conduction band and the positively charged holes in the valence band.

The total electron-hole Hamiltonian, in the presence of a dipole coupling, reads:

$$H(t) = \sum_{\mathbf{k}} \left(E_{c,\mathbf{k}} e_{\mathbf{k}}^\dagger e_{\mathbf{k}} + E_{h,\mathbf{k}} h_{\mathbf{k}}^\dagger h_{\mathbf{k}} - E_0(t) \hat{\epsilon} \cdot \mathbf{d}_{cv} e_{\mathbf{k}}^\dagger h_{-\mathbf{k}}^\dagger \right) +$$
$$\frac{1}{2} \sum_{\mathbf{k},\mathbf{k}'} \sum_{\mathbf{q} \neq \mathbf{0}} V_q \left(e_{\mathbf{k}+\mathbf{q}}^\dagger e_{\mathbf{k}'-\mathbf{q}}^\dagger e_{\mathbf{k}'} e_{\mathbf{k}} + h_{\mathbf{k}+\mathbf{q}}^\dagger h_{\mathbf{k}'-\mathbf{q}}^\dagger h_{\mathbf{k}'} h_{\mathbf{k}} - 2 e_{\mathbf{k}+\mathbf{q}}^\dagger h_{\mathbf{k}'-\mathbf{q}}^\dagger h_{\mathbf{k}'} e_{\mathbf{k}} \right) \tag{129}$$

We define the following correlators:

$$n_{e,\mathbf{k}}(t) = \langle e_{\mathbf{k}}^\dagger e_{\mathbf{k}} \rangle, \quad n_{h,\mathbf{k}}(t) = \langle h_{-\mathbf{k}}^\dagger h_{-\mathbf{k}} \rangle, \quad P_{\mathbf{k}}(t) = \langle h_{-\mathbf{k}} e_{\mathbf{k}} \rangle. \tag{130}$$

The minus signs at the indices of the hole operators take into account that $n_{h,\mathbf{k}} + n_{e,\mathbf{k}}$ remains constant during a direct interband excitation.

B. Equations of motion (SBE)

As we already did (partly) in the lecture on excitons, we now derive Heisenberg equations of motion for the pair correlations and the occupations:

$$i\hbar \frac{d}{dt} \langle O \rangle = \langle [O, H(t)] \rangle. \tag{131}$$

This leads to:

$$\frac{d}{dt} P_{\mathbf{k}} = -i \left(E_{e,\mathbf{k}} - E_{h,\mathbf{k}} \right) P_{\mathbf{k}} - \frac{i}{\hbar} (n_{e,\mathbf{k}} + n_{h,\mathbf{k}} - 1) \hat{\epsilon} \cdot \mathbf{d}_{cv} E_0(t)$$
$$- \frac{i}{\hbar} \sum_{\mathbf{k}'} \sum_{\mathbf{q} \neq \mathbf{0}} V_q \Big[\langle e_{\mathbf{k}+\mathbf{q}}^\dagger h_{-\mathbf{k}+\mathbf{q}} e_{\mathbf{k}'} e_{\mathbf{k}} \rangle - \langle e \leftrightarrow h \rangle$$
$$+ \langle h_{-\mathbf{k}} e_{\mathbf{k}'-\mathbf{q}}^\dagger e_{\mathbf{k}'} e_{\mathbf{k}-\mathbf{q}} \rangle - \langle e \to h \rangle \Big]. \tag{132}$$

and

$$\frac{d}{dt} n_{e,\mathbf{k}} = -\frac{2}{\hbar} \text{Im} \left[\hat{\epsilon} \cdot \mathbf{d}_{cv} E_0(t) P_{\mathbf{k}}^* \right]$$
$$+ \frac{i}{\hbar} \sum_{\mathbf{k}'} \sum_{\mathbf{q} \neq \mathbf{0}} V_q \Big[\langle e_{\mathbf{k}}^\dagger e_{\mathbf{k}'-\mathbf{q}}^\dagger e_{\mathbf{k}-\mathbf{q}} e_{\mathbf{k}'} \rangle - \langle \mathbf{k} \to \mathbf{k}+\mathbf{q} \rangle$$
$$\langle e_{\mathbf{k}}^\dagger e_{\mathbf{k}-\mathbf{q}} h_{\mathbf{k}'-\mathbf{q}}^\dagger h_{\mathbf{k}'} \rangle - \langle \mathbf{k} \to \mathbf{k}+\mathbf{q} \rangle \Big]. \tag{133}$$

The equation for $n_{h,\mathbf{k}}$ is of the same form (essentially with e and h exchanged).

Again we proceed by splitting the 4-operator products into products of 2-operator products, and explicitly keep only the mean-field / Hartree-Fock / RPA terms, i.e. those where at least one 2-operator product is an occupation number (i.e. diagonal):

$$\frac{d}{dt} P_{\mathbf{k}} = -\frac{i}{\hbar} (E_{e,\mathbf{k}} - E_{h,\mathbf{k}}) P_{\mathbf{k}} - \frac{i}{\hbar} (n_{e,\mathbf{k}} + n_{h,\mathbf{k}} - 1) \left[\hat{\epsilon} \cdot \mathbf{d}_{cv} E_0(t) + \sum_{\mathbf{q} \neq \mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} P_{\mathbf{q}} \right] + \left. \frac{\partial P_{\mathbf{k}}}{\partial t} \right|_{\text{scatt}}, \tag{134}$$

and

$$\frac{d}{dt} n_{e,\mathbf{k}} = -\frac{2}{\hbar} \text{Im} \left\{ \left[\hat{\epsilon} \cdot \mathbf{d}_{cv} E_0(t) + \sum_{\mathbf{q} \neq \mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} P_{\mathbf{q}} \right] P_{\mathbf{k}}^* \right\} + \left. \frac{\partial n_{e,\mathbf{k}}}{\partial t} \right|_{\text{scatt}}, \tag{135}$$

and

$$\frac{d}{dt} n_{h,\mathbf{k}} = -\frac{2}{\hbar} \text{Im} \left\{ \left[\hat{\epsilon} \cdot \mathbf{d}_{cv} E_0(t) + \sum_{\mathbf{q} \neq \mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} P_{\mathbf{q}} \right] P_{\mathbf{k}}^* \right\} + \left. \frac{\partial n_{h,\mathbf{k}}}{\partial t} \right|_{\text{scatt}}. \tag{136}$$

The last term in each of these equations, the "scattering" term, may take into account the scattering terms which are beyond mean-field, or other dissipative terms. We note that, on the mean-field level, this set of equations is closed, i.e. it fully determines the dynamics of the mean-field system. We can further simplify the notation by introducing a *generalized Rabi frequency*:

$$\omega_{R,\mathbf{k}} = \frac{1}{\hbar}\left(\hat{\epsilon}\cdot\mathbf{d}_{cv}E_0(t) + \sum_{\mathbf{q}\neq\mathbf{k}}V_{|\mathbf{k}-\mathbf{q}|}P_{\mathbf{q}}\right). \tag{137}$$

With this, the equations of motion are written compactly in the form known as *semiconductor Bloch equations*:

$$\frac{d}{dt}P_{\mathbf{k}} = -\frac{i}{\hbar}(E_{e,\mathbf{k}} - E_{h,\mathbf{k}})P_{\mathbf{k}} - i(n_{e,\mathbf{k}} + n_{h,\mathbf{k}} - 1)\omega_{R,\mathbf{k}} + \left.\frac{\partial P_{\mathbf{k}}}{\partial t}\right|_{\text{scatt}}, \tag{138}$$

and

$$\frac{d}{dt}n_{e,\mathbf{k}} = -\frac{2}{\hbar}\text{Im}\{\omega_{R,\mathbf{k}}P_{\mathbf{k}}^*\} + \left.\frac{\partial n_{e,\mathbf{k}}}{\partial t}\right|_{\text{scatt}}, \tag{139}$$

and

$$\frac{d}{dt}n_{h,\mathbf{k}} = -\frac{2}{\hbar}\text{Im}\{\omega_{R,\mathbf{k}}P_{\mathbf{k}}^*\} + \left.\frac{\partial n_{h,\mathbf{k}}}{\partial t}\right|_{\text{scatt}}. \tag{140}$$

These equations determine the optical properties of semiconductors. They are valid in various regimes (low- or high-excitation, quasi-equilibrium or ultrafast regime, linear or non-linear). Applications of these equations include the description of pump-probe experiments and wave-mixing spectroscopy, high-harmonic generation, linear or non-linear response of excitons, etc.

Often one is interested in how light propagates through a crystal. Also in this case, the semiconductor Bloch equations determine the response of the crystal to the light, but in addition one may use the crystal polarization P as a source term to Maxwell equations. In this case, semiconductor Bloch equations and Maxwell's wave equation have to be solved self-consistently:

$$\frac{\partial^2 E}{\partial t^2} - \frac{c^2}{n_0^2}\Delta E = -4\pi\frac{\partial^2 P}{\partial t^2}, \tag{141}$$

with n_0 the refractive index of the unexcited crystal.

C.   Application of the SBEs: Non-linear response of excitons

Without the scattering terms the semiconductor Bloch equations are diagonal in $\mathbf{k}$, and with this, formally equivalent to the Bloch equations describing a two-level system. The complicated mixing of wave vectors due to interactions is included, in a very simple way, within the generalized Rabi frequency and within the effective masses (band energies containing self-exchange energy).

The Bloch equations of a two-level system read:

$$i\frac{d}{dt}P = \epsilon P - (1 - 2n)\frac{d_{21}}{\hbar}E(t), \quad i\frac{d}{dt}n = -\frac{1}{\hbar}(d_{21}E(t)P^* - \text{c.c.}). \tag{142}$$

Here, $P = \langle a_1^\dagger a_2\rangle$, $n = n_2 = \langle a_2^\dagger a_2\rangle = 1 - n_1$, $\epsilon = E_1 - E_2$.

These equations have a conserved quantity:

$$K = (1 - 2n)^2 + 4|P|^2. \tag{143}$$

Choosing as initial conditions the unexcited crystal, $P = 0$ and $n = 0$, we have $K = 1$, or

$$n = \frac{1}{2}\left(1 \pm \sqrt{1 - 4|P|^2}\right). \tag{144}$$

If the field is switched on adiabatically, only the minus sign can be realized. In the low-excitation regime, $P \ll 1$, we find by expansion in P:

$$n = |P|^2 + \mathcal{O}(|P|^4). \tag{145}$$

We can immediately map this result onto the coherent semiconductor Bloch equations: $n_{e,\mathbf{k}} = n_{h,\mathbf{k}} = |P_\mathbf{k}|^2$.

With this, the equation of motion for $P_\mathbf{k}$ becomes formally independent from $n_{i,\mathbf{k}}$. If we take this relation between $n_{i,\mathbf{k}}$ and $|P_\mathbf{k}|^2$ into account also in the self-interaction terms in the energies $E_{i,\mathbf{k}}$, given by $-\sum_{\mathbf{q} \neq \mathbf{0}} V_q n_{i,\mathbf{k}-\mathbf{q}}$, the equation of motion becomes:

$$\frac{d}{dt} P_\mathbf{k} = -\frac{i}{\hbar} \left[\left(E_{\text{gap}} + \frac{\hbar^2 k^2}{2\mu} \right) P_\mathbf{k} - \sum_{\mathbf{q} \neq \mathbf{0}} V_q P_{\mathbf{k}-\mathbf{q}} \right] + \frac{i}{\hbar} (1 - 2|P_\mathbf{k}|^2) \hat{\epsilon} \cdot \mathbf{d}_{cv} E_0(t)$$
$$+ 2 \frac{i}{\hbar} \sum_{\mathbf{q} \neq \mathbf{k}} V_q P_{\mathbf{k}-\mathbf{q}} (P_{\mathbf{k}-\mathbf{q}}^* - P_\mathbf{k}^*) P_\mathbf{k}. \tag{146}$$

The first term on the rhs is exactly the one which we had already encountered in the Wannier equation. The second and the third term contain non-linearities in $P_\mathbf{k}$. The second term is the inhomogeneous part of the Bethe-Salpeter equation, but instead of being a constant $d_{cv} E_0(t)$ it is now proportional to $(1 - 2|P_\mathbf{k}|^2)$. This dependence accounts for *phase-space filling*: Excitation in the crystal reduce the number of available states, thus decreasing the optical coupling. The third term, of third order in $P_\mathbf{k}$ describes exciton-exciton interactions.

Assuming that the polarization is dominated by the 1s excitonic state $\varphi_{1s}(k)$, we may make the following ansatz:

$$P_\mathbf{k} = \Psi(t) \varphi_{1s}(k). \tag{147}$$

Inserting in Eq. (146), multiplying with $\varphi_{1s}(k)$, and summing over all k, we get a non-linear Schroedinger equation for $\Psi(t)$:

$$i\hbar \frac{d}{dt} \Psi = (E_{\text{gap}} + E_{1s}) \Psi - \varphi_{1s}^*(r=0) \hat{\epsilon} \cdot \mathbf{d}_{cv} E_0(t) + 2\hat{\epsilon} \cdot \mathbf{d}_{cv} E_0(t) |\Psi|^2 \sum_k |\varphi_{1s}(k)|^2 \varphi_{1s}^*(k)$$
$$+ 2|\Psi|^2 \Psi \sum_k V_q |\varphi_{1s}(k)|^2 [\varphi_{1s}^*(k) - \varphi_{1s}^*(k-q)] \varphi_{1s}(k-q). \tag{148}$$

As we already did in the second lecture, non-linear equations can be solved iteratively. That is, we first obtain the first-order solution $\Psi^{(1)}$ by neglecting the non-linear terms:

$$(\hbar\omega - E_{\text{gap}} - E_{1s}) \Psi^{(1)} e^{i\omega t} = -\varphi_{1s}^*(r=0) \hat{\epsilon} \cdot \mathbf{d}_{cv} E_0 e^{i\omega_0 t}, \tag{149}$$

$$\Rightarrow \Psi^{(1)} = \frac{\varphi_{1s}^*(r=0) \hat{\epsilon} \cdot \mathbf{d}_{cv} E_0}{\Delta}, \tag{150}$$

where $\Delta = E_{\text{gap}} + E_{1s} - \hbar\omega_0$.

Then we plug in the solution of the linearized system into the higher-order terms to obtain non-linear corrections:

$$\Psi^{(3)} = 2 \frac{|\varphi_{1s}^*(0)|^2 (\hat{\epsilon} \cdot \mathbf{d}_{cv})^3 E_0^3}{\Delta^3} \sum_k |\varphi_{1s}(k)|^2 \varphi_{1s}^*(k)$$
$$+ 2 \frac{\varphi_{1s}^*(0) |\varphi_{1s}^*(0)|^2 (\hat{\epsilon} \cdot \mathbf{d}_{cv})^3 E_0^3}{\Delta^4} \sum_k V_q |\varphi_{1s}(k)|^2 [\varphi_{1s}^*(k) - \varphi_{1s}^*(k-q)] \varphi_{1s}(k-q) \tag{151}$$

This is proportional to the third-order susceptibility, that is, we found a response function beyond linear response.

D. Microscopic model for damping: Boltzmann scattering rates

The scattering terms in the semiconductor Bloch equations may be used to account for relaxation. A simple phenomeological description could be:

$$\left. \frac{\partial dn_{e,\mathbf{k}}}{\partial t} \right|_{scatt} = \frac{f_{e,\mathbf{k}} - n_{e,\mathbf{k}}(t)}{T_{\text{intra}}} - \frac{n_{e,\mathbf{k}}(t)}{T_{\text{inter}}}. \tag{152}$$

If we sum over all $\mathbf{k}$, the first term on the right-hand side vanishes, so it describes relaxation in the band towards an equilibrium distribution $f_{e,\mathbf{k}}$. The second term describes recombination.

The microscopic processes which lead to relaxation include carrier-carrier scattering, scattering of carriers with impurities, or with different phonon modes. Which of these processes is the fastest, depends on the material and on the amount of excitation. In the low-excitation regime, scattering with LO phonons usually leads to fast relaxation. A simple microscopic model for such processes is the Froehlich Hamiltonian:

$$H_{\mathrm{F}} = \sum_{i=c,v} \sum_{\mathbf{k},\mathbf{q}} \hbar g_{\mathbf{q}} a_{i,\mathbf{k}+\mathbf{q}}^{\dagger} a_{i,\mathbf{k}} (b_{\mathbf{q}} + b_{-\mathbf{q}}), \tag{153}$$

where $b_{\mathbf{q}}$ are bosonic operators annihilating one phonon at wave vector $\mathbf{q}$. The coupling strength $g_{\mathbf{q}}$ can be related to the dielectric constant of the crystal, and is typically weak compared to the phonon energy (typically on the order of 20-40 meV). With the phonons being optical, their dispersion is rather flat, and we may assume a constant phonon energy: $H_{LO} = \sum_{\mathbf{q}} \hbar\omega_0 b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}}$.

The scattering terms are then defined as:

$$\left.\frac{\partial \rho_{i,j}(\mathbf{k})}{\partial t}\right|_{scatt} = \frac{i}{\hbar} \langle [H_{\mathrm{F}}, a_{i,\mathbf{k}}^{\dagger} a_{j,\mathbf{k}}] \rangle. \tag{154}$$

The rhs can be expressed in terms electron-phonon correlators of the type

$$F_{ij,\mathbf{k},\mathbf{q}} = \langle a_{j,\mathbf{k}+\mathbf{q}}^{\dagger} a_{i,\mathbf{k}} b_{\mathbf{q}} \rangle, \tag{155}$$

and three other correlators obtained by changing $b_{\mathbf{q}}$ to $b_{-\mathbf{q}}^{\dagger}$, and changing the index $\mathbf{k}$ to index $\mathbf{k} - \mathbf{q}$. Physically, these four correlators describe processes where either the electronic $\mathbf{k}$-level decays into another level under emission or absorption of a phonon, or there is decay into the $\mathbf{k}$-level under emission or absorption of a phonon, see also Fig. 5.

We now could try to determine the equation of motion for these correlators using the full Hamiltonian (band energies, Coulomb interactions, light-matter coupling, phonon energy, electron-phonon coupling), but that's too ambitious. Let us keep things more simple, and consider only electron-phonon coupling. Moreover, we restrict ourselves to scattering terms in the diagonal terms (i.e. for the occupations, but not correlations).

It then becomes straightforward to integrate the equation of motion for $F_{ii,\mathbf{k},\mathbf{q}}(t)$, and for the other three correlators. Introducing some notation, with this we can write the scattering terms in the following way:

$$\left.\frac{\partial n_{i,\mathbf{k}}}{\partial t}\right|_{scatt} = - \sum_{\mathbf{q}} \sum_{\sigma=\pm 1} \sigma g_{\mathbf{q}}^2 \int_{-\infty}^{t} dt' \; e^{i(E_{i,\mathbf{k}+\sigma\mathbf{q}} - E_{i,\mathbf{k}} - \sigma\omega_0 + i\gamma)(t-t')} \Big\{ N_{\sigma} n_{i,\mathbf{k}}(t')[1 - n_{i,\mathbf{k}+\sigma\mathbf{q}}(t')]$$
$$- [N_{\sigma} + 1] n_{i,\mathbf{k}+\sigma\mathbf{q}}(t')[1 - n_{i,\mathbf{k}}(t')] \Big\} - \{\mathbf{k} \leftrightarrow \mathbf{k} - \sigma\mathbf{q}\}, \tag{156}$$

where $N_{\sigma} = (e^{\beta\hbar\sigma\omega_0} - 1)^{-1}$ is the number of thermal phonons at frequency $\sigma\omega_0$. The temporal integral in this expression keeps memory, so the dynamics is non-Markovian. This is particularly relevant on short time scales, where the dynamics is called *quantum kinetics*. On the other hand, if $t\omega_0 \gg 1$, the integrand oscillates rapidly, and we may take out everything but the exponential from the integration. Then the temporal integral just leads to a Kronecker-delta (energy conservation), and we have obtained *Markovian dynamics*.

In this Markovian approximation, the scattering rates are known as *Boltzmann scattering rates*:

$$\left.\frac{\partial n_{i,\mathbf{k}}}{\partial t}\right|_{scatt} = -2\pi \sum_{\mathbf{q}} g_{\mathbf{q}}^2 \delta(E_{i,\mathbf{k}+\mathbf{q}} - E_{i,\mathbf{k}} - \omega_0) \Big[N_{\mathbf{q}} n_{i,\mathbf{k}}(1 - n_{i\mathbf{k}+\mathbf{q}}) - (N_{\mathbf{q}} + 1) n_{i,\mathbf{k}+\mathbf{q}}(1 - n_{i\mathbf{k}}) \Big]$$
$$-2\pi \sum_{\mathbf{q}} g_{\mathbf{q}}^2 \delta(E_{i,\mathbf{k}-\mathbf{q}} - E_{i,\mathbf{k}} - \omega_0) \Big[(N_{\mathbf{q}} + 1) n_{i,\mathbf{k}}(1 - n_{i\mathbf{k}-\mathbf{q}}) - N_{\mathbf{q}} n_{i,\mathbf{k}-\mathbf{q}}(1 - n_{i\mathbf{k}}) \Big]. \tag{157}$$

These four terms correspond to the four scattering processes sketched in Fig. 5.
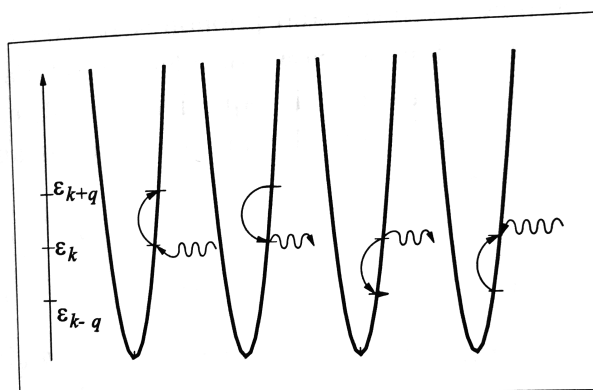
FIG. 5: Sketch of four different electron-phonon scattering processes which contribute to the Boltzmann scattering rate. Taken from: Haug and Koch, "Quantum Theory of the Optical and Electronic Properties of Semiconductors", 2nd ed. (2004).